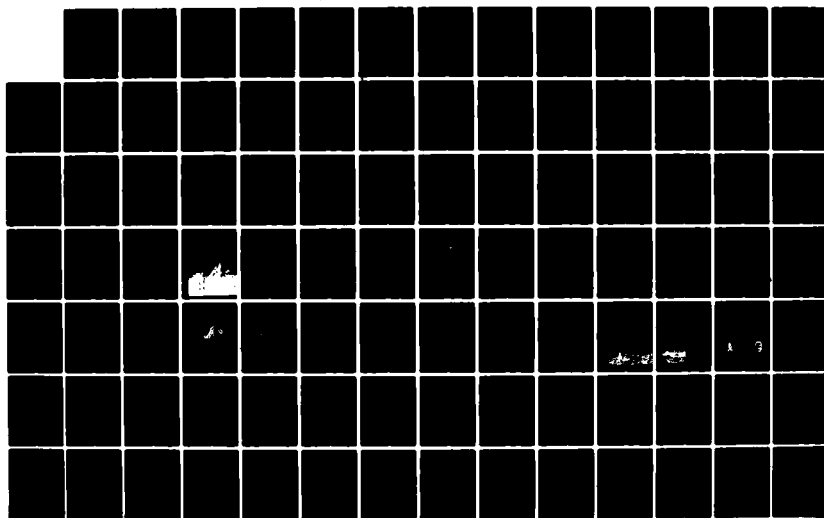AD-A134 263   ARCTIC HAZE: NATURAL OR POLLUTION?(U) RHODE ISLAND UNIV   1/2
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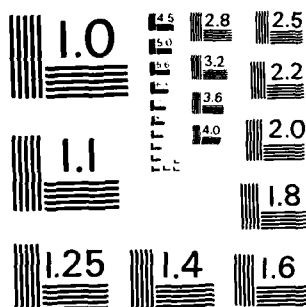   K A RAHN ET AL. AUG 83 N00014-76-C-0435

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Routine aerosol sampling at Barrow and Fairbanks continued. The basic four-year record of certain constituents in the Barrow aerosol showed ditinct and reproducible seasonal variations. Cascade-impactor samples from Barrow and Europe were taken and analyzed for sulfate and trace elements. SO$_2$ at Bear Island during winter was found to be highly pulsed and associated mainly with cyclonic trajectories from eastern Europe and the USSR. On the basis of a wide variety of indirect meteorological and chemical evidence, Eurasia was strongly suggested to be the major source of Arcitc haze, with North

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America contributing only occasionally. Aerosol sampling at Iceland continued. Aerosol was sampled at western Ireland during winter 1980-81 and the following summer. A cooperative European Aerosol-Sampling Network was established and has proved highly successful. The hypothesis of the Eurasian source of Arctic haze was confirmed by the noncrustal Mn/V ratio, the first regional tracer for pollution aerosol; the dominance of Eurasian sources was further confirmed by a much more sophisticated seven-element tracer system which proved capable of discriminating among regional aerosols in Europe and North America. Elemental data from eastern North America were used to help understand the sources and transport of pollution aerosol there. The signature of aerosol from the Noril'sk smelting complex was developed, and found only once in 50 samples at Barrow. Pollution aerosol from midlatitudes was found to increase concentrations of cloud-condensation nuclei in the Arctic but decrease concentrations of ice nuclei. Papers from the Second Symposium on Arctic Air Chemistry were published in a special issue of Atmospheric Environment (8/80); plans for the second symposium were made. A cooperative study with W. Berg of NCAR on Arctic bromine was begun. Examination of the records of the "Ptramigan" weather reconnaissance flights showed that their haze observations had a seasonal variation similar to that of modern pollution aerosol.at Barrow.

ARCTIC HAZE: NATURAL OR POLLUTION?

A Progress Report and Renewal Proposal to the
Office of Naval Research
Arctic Program

August 1983

Graduate School of Oceanography
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Narragansett, Rhode Island 02882-1197

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Fairbanks, Alaska 99701

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Statement of Submission

The following progress report and renewal proposal, "Arctic Haze: Natural or Pollution?", is hereby submitted to the Office of Naval Research, Arctic Program, for consideration as an extension of Contract N00014-76-C-0435, of the same title. The progress report covers work done jointly by the University of Rhode Island and the University of Alaska; the renewal proposal is for the University of Rhode Island alone.

This proposal is not being submitted to any other agency for financial support, although certain costs are to be shared with other grants and contracts awarded to the University of Rhode Island.

ABSTRACT

A three-year program of continued research into the chemical and meteorological aspects of Arctic haze is planned. The principal focus will be on extending and refining our new system of regional elemental tracers for pollution aerosol and using it to better understand the sources and transport of Arctic haze. Raw data for the tracer system will come from continued analysis of aerosol samples at Barrow, at several sites in the Norwegian Arctic (in cooperation with the Norwegian Institute for Air Research), the NOAA/ONR AGASP aircraft-sampling program, various cooperative sites in Europe, and continued aircraft samples from the Eurasian Arctic. All samples will be analyzed for trace elements by neutron activation and atomic absorption and for sulfate by turbidimetry. The project on particle-size distributions of the Barrow aerosol will be concluded. The cooperative study of Arctic bromine with the National Center for Atmospheric Research will continue. The Third Symposium on Arctic Air Chemistry will be organized jointly with the Canadian Atmospheric Environment Service. As a result of these efforts, we should have an elemental tracer system which will reveal with much greater precision area sources, point sources, and transport pathways of pollution aerosol in the Arctic. As a fringe benefit, we will understand sources and transport of aerosol in and around Europe with the same improved precision.

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I.   Progress Report - August 1980-July 1983 (URI, UA)

A.   Highlights of activities and results

1.   Activities

- Routine aerosol sampling at Barrow and Fairbanks continued. At Barrow, the samples were daily during winter 1980-81, winter 1981-82, and March-April 1983, semi-weekly otherwise. At Fairbanks, samples were weekly.

- After establishing a basic four-year record of aerosol at Barrow, subsequent analysis has been selective.

- Cascade-impactor samples from Barrow and Europe were taken and analyzed for sulfate and trace elements (Lewis M.S. thesis, URI).

- Aerosol sampling at Iceland continued. After the initial period of weekly samples, they were taken every two days.

- Aerosol was sampled at western Ireland during winter 1980-81 and the following summer.

- A cooperative European Aerosol-Sampling Network was established, and provided samples during 1981 and 1982. Sites were in Belgium, Germany, Austria, Hungary, Sweden and Finland.

- Analysis and interpretation of aerosol samples from eastern North America led the URI group into a substantial involvement with the acid-precipitation question there.

- Papers from the Second Symposium on Arctic Air Chemistry were published in a special issue of Atmospheric Environment (August 1981) with K. Rahn as guest editor.

- Plans were made for the Third Symposium on Arctic Air Chemistry, to be held May 1984 in Toronto, with L.A. Barrie as host and K. Rahn as chairman.

- T. Conway, R. Borys and W. Raatz participated in the summer 1980 YMER-80 cruise in the Norwegian Arctic.

- The Ph.D. theses of R. Borys (Colorado State University) and W. Raatz (University of Alaska) were completed.

- A cooperative program with W. Berg of NCAR on Arctic bromine was begun.

. Plans for a joint program with the Soviet Union on USSR aerosol were made, through the US-USSR Bilateral Agreement on Protection of the Environment.

. K. Rahn was invited to visit the People's Republic of China for 3 weeks in September 1983. A joint program on elemental tracers of Chinese aerosol is likely to result.

. A cooperative program with the Air Force was established for analysis of aircraft samples of aerosol from the Eurasian Arctic.

. K. Rahn, R. Borys, G. Shaw and W. Raatz participated in the NOAA/ONR aircraft-based Arctic Gas and Aerosol Sampling Program during March and April 1983.

. A cooperative program with the Norwegian Institute for Air Research was begun, under which URI will analyze samples taken by NILU at various points in the Norwegian Arctic.

. A diffusion battery and sensitive particle counter for measuring particle-size distributions throughout the Aitken range was constructed at UA and used extensively outside Fairbanks.

. Further optical measurements were taken in Fairbanks, Barrow, and the Norwegian Arctic.

. Using an electron microscope, single aerosol particles from Alaska and the Norwegian Arctic were analyzed for a variety of major and minor elements.

. The photo-reactivity of air and air doped with various gases was investigated outside Fairbanks.

. The records of haze from the Ptarmigan weather-reconnaissance flights were examined statistically.

2. **Results**

. The basic four-year record of certain constituents in the Barrow aerosol showed distinct and reproducible seasonal variations.

. SO_2 at Bear Island during winter was found to be highly pulsed and associated mainly with cyclonic trajectories from eastern Europe and the USSR. Long residence times were inferred.

. On the basis of a wide variety of indirect meteorological and chemical evidence, Eurasia was strongly suggested to be the major source of Arctic haze, with North America contributing only occasionally.

- This was confirmed by the noncrustal Mn/V ratio, the first regional tracer for pollution aerosol to be developed. Values in the Arctic were compatible with Eurasian sources and incompatible with eastern North American sources.

- The dominance of Eurasian sources was further confirmed by a much more sophisticated seven-element tracer system which proved capable of discriminating among regional aerosols in Europe and North America even after long-range transport. At least 80% of the aerosols at Barrow and 95% of those at Bear Island were Eurasian in origin.

- Elemental data from eastern North America were used to help understand the sources and transport of pollution aerosol there, from the standpoint of acid deposition. They revealed that the Northeast was exposed to a wider variety of aerosols than previously recogni? and that sources for coastal sites were very different from those for interior sites.

- The signature of aerosol from the Noril'sk smelti complex was developed, and found only once in 50 samples at Barrow. When present, it affected a f trace elements, not the bulk of the haze aerosol.

- "Black" and "white" episodes of pollution aerosol in Europe were shown to be early stages of a general atmospheric aging process which leads ultimately to the characteristics observed in Arctic aerosol.

- Pollution aerosol from midlatitudes increases the concentrations of cloud-condensation nuclei in the Arctic but decreases the concentrations of ice nuclei.

- Clouds in polluted Arctic air masses may have fewer ice crystals but more liquid drops than clouds in unpolluted Arctic air. The "polluted" clouds would thus be more colloidally stable and optically thicker than otherwise.

- The strange spring maximum in atmospheric bromine at Barrow was studied further. Via a cooperative program with NCAR, it was shown that the levels of total Br (gaseous plus particulate) at that time are the highest observed anywhere. A natural marine source seems likely.

- Aircraft samples from the Eurasian Arctic allowed elemental signatures for point and area sources within the Soviet Union to be developed, and showed that this area was the source for much of the pollution aerosol found at Barrow.

. An eddy-diffusion model predicted the sulfate concen-
trations in the Arctic atmosphere to within a factor
of two and suggested that Arctic cloudiness was the
dominant factor in producing the tenfold seasonal
variations in Arctic pollution aerosol.

. Optical measurements have confirmed that the single-
scattering albedo for the Arctic aerosol is low
(0.6-0.8), because of its large soot content. This
supports the earlier deduction that pollution aerosol
in the Arctic warms the lower atmosphere during
spring.

. A spring maximum in atmospheric turbidity was found
for the Fairbanks area, in near-coincidence with the
better-known spring maximum at Barrow. The Fairbanks
maximum is associated with outbreaks of Arctic air
from the North.

. Analysis of individual aerosol particles from the
Norwegian Arctic showed that the larger particles were
predominantly sea salt and soil, whereas the smaller
particles were strongly sulfurous.

. Particles entering central Alaska from the Pacific had
unimodal size spectra, with a particle maximum near
radius 10^{-2} μm and relatively large numbers
(300-2000 cm^{-3}); particles entering from the Arctic
had bimodal distributions (maxima at radii $3x10^{-3}$
and $5x10^{-2}$ μm), lower numbers (150-700 cm^{-3}), but
twice the mass in the submicron range.

. It was found that large numbers of tiny particles are
produced when Pacific air at Fairbanks is irradiated
with ultraviolet light, whereas Arctic air near
Fairbanks showed no such effect.

. Meteorological analysis suggested that transport of
aerosol from Eurasia to Alaska is controlled more by
anticyclones than by cyclones. The zone of greatest
transport may be in the area of strong pressure
gradient along the edge of quasi-stationary
anticyclones.

. Examination of the records of the "Ptarmigan" weather
reconnaissance flights showed that their haze obser-
vations had a seasonal variation similar to that of
modern pollution aerosol at Barrow. Haze observations
during summer may have been caused occasionally by
Asian desert dust.

B.   Activities

1.   Routine aerosol sampling in Alaska.

Throughout our Arctic Haze project, we have sampled surface aerosol continuously at Barrow, Alaska because of the valuable information contained in these samples. We are now approaching seven years of sampling; our tentative plan is to continue until the record is ten years long (at the end of the period covered by this renewal proposal).

Originally, we sampled weekly. Because of the high levels of pollution aerosol encountered during the first winter at Barrow, we felt confident in switching to semi-weekly samples the second winter. Beginning in 1979-80, we collected daily samples during winter and semi-weekly samples during summer. Last winter (1982-83), because the backlog of samples was so great, we switched back to semi-weekly samples. At this point, we plan to continue the semi-weekly schedule except for special events.

The first four years of samples have been analyzed for sulfate by turbidimetry and trace elements by short-lived neutron activation. One winter has been analyzed for additional elements by long-lived neutron activation. Currently, additional samples from Barrow are now being archived for selective analysis later. This is quite acceptable to NOAA/GMCC, which collects them for us.

At Fairbanks, sampling is weekly and the samples are archived.

2.   Analysis of cascade-impactor samples from Barrow and points in Europe (Lewis M.S. thesis, URI).

For her Master's thesis, N.F. Lewis of URI had six cascade impactors fabricated and sent to Europe and the Arctic. During the winter of 1981-82, six week-long samples were taken for her at Barrow, as well as seven others from Sweden and West Germany. These samples are now completely analyzed, and her thesis is being written. The defense is expected in September or October 1983. The project has been a success.

3.   Aerosol sampling in Iceland

Thanks to the patience and cooperativeness of the Icelandic Meteorological Office, aerosol sampling in Iceland has continued in an unbroken fashion during the past three years. We have analyzed only a portion of the samples, but have been able to show that pollution aerosol there is predominantly European, not North American. A variety of strong episodes from Europe has been detected, both during summer and winter. No cases of transport from North America have been detected. We expect to continue this program for at least 1-2 years more.

4.   Aerosol sampling in western Ireland

As part of our prog· n to study possible trans-
Atlantic transport of aerosol from North America to Europe and the
Arctic, we arranged for a series of aerosol samples to be taken for us in
the Aran Islands, just outside Galway Bay in western Ireland. Through
the courtesy of Dr. Edward Monahan, an ONR contractor at the Department
of Oceanography in University College Galway, we received samples during
winter 1980-81 and summer 1981. Analysis of these samples showed clearly
that all air masses from the Atlantic were clean, and thus agreed with
our data from Iceland that trans-Atlantic transport of aerosol could not
be detected near the surface.

We are now completing the analysis of these samples, and expect to
use them to help establish trace-elemental signatures from the United
Kingdom aerosol. Our signatures from the U.K. are not as well-developed
as are those from western Europe proper.

5.   The URI European Aerosol-Sampling Network

In 1981 we established the cooperative URI European
Aerosol-Sampling Network, for the dual purpose of examining the
variations in signatures in and around Europe and learning once and for
all whether Europe was really the source of Arctic aerosol. We managed
to enlist help from six countries, and obtained aerosol samples from
Ghent, Belgium; Mainz and West Berlin, West Germany; Kecskemet and
Budapest, Hungary; Rorvik, Sweden; and Ahtari, Finland. These sites
operated for various periods in 1981-83. With the help of additional
samples from Ireland, Iceland, France, Norway and the Norwegian Arctic,
we are well on our way to formulating a detailed picture of European
aerosol and how it moves.

This project has succeeded beyond our wildest dreams. Some of its
results are discussed in Sections I.C.5 and I.E.5.

6.   Sources of acid rain in eastern North America

Although this aspect of our work is not a true Arctic
topic, it represents such an interesting and (we believe) significant
spinoff that we mention it here. Approximately two years ago, we set
out to use our new noncrustal Mn/V ratio to confirm that the Midwest was
a major source of pollution aerosol for the East Coast. Recall that the
noncrustal Mn/V ratio was developed originally to discriminate between
aerosol from eastern North America and Europe. Knowing that the Mn/V
ratio of midwestern aerosol was an order of magnitude higher than that of
northeastern aerosol, we reasoned that pulses of aerosol from the Midwest
should have higher Mn/V ratios than the more local aerosol before or
after the pulses. Using three years of data from Rhode Island, we were
unable to find higher Mn/V ratios associated with pollution episodes in
summer. Instead, we found northeastern ratios throughout the episodes.
Near-midwestern Mn/V ratios were found only in winter, and then rarely
and under nonepisodic conditions.

At the urging of colleagues, we released these findings in an open letter of 21 November 1981. Others distributed this letter widely, and elemental tracers have been in the news ever since.

In the interim, we have refined our tracer system and broadened our geographical coverage of the Northeast. We now see clearly that sources and transport are very different for the coastal Northeast than for the interior Northeast. The classical picture of dominant midwestern sources of sulfate and acidity holds reasonably well for the interior, but much less so for the coast. The great importance of these results is that they offer a more direct and reliable picture of sources and transport of aerosol than is available otherwise, i.e., through long-range transport models. We hope that they will help lead to a control program for SO_2 which is balanced rather than being slanted unduly toward any particular region.

One beneficial aspect of this whole experience is that it allowed us to collect considerably more trace-element data from North America than we would have otherwise. The North American regional signatures have been useful in formulating a general picture of elemental tracers (see the Science preprint in Section I.E.5).

7. The Arctic issue of Atmospheric Environment

Twenty-one papers from the Second Symposium on Arctic Air Chemistry, held at URI 6-8 May 1980, were published together in a special issue of Atmospheric Environment dated August 1981. K. Rahn served as Guest Editor. These papers have given Arctic air chemistry a visibility and respectability that it did not have before, and signaled the beginning of general acceptance for the ideas which we had championed for several years. Now the field has a momentum of its own; we need no longer push and prod.

8. Plans for the Third Symposium on Arctic Air Chemistry

The Third Symposium on Arctic Air Chemistry is now being planned. It will be held 7-9 May 1984 (four years after the Second Symposium) in Downsview, Ontario. Dr. L.A. Barrie of the Canadian Atmospheric Environment Service will be host; K.A. Rahn will be chairman. We expect the symposium to be very well attended. It will be sponsored entirely by the Canadian government.

9. Participation in YMER-80.

During June-September 1980, three members of our project (T. Conway, R. Borys, W. Raatz) participated in the cruise of the Swedish icebreaker YMER in the waters of the Norwegian Arctic. K. Rahn had attended an earlier planning meeting in Stockholm. T. Conway and R. Borys took aerosol samples from the ship; W. Raatz took air samples and optical measurements for G. Shaw from Kungsoya. Dr. Borys' measurements formed part of his thesis; Raatz-Shaw's data have appeared in part in an Atmospheric Environment article on single-particle analysis of polar aerosols. In general, the YMER-80 measurements have confirmed that the Norwegian Arctic is extremely clean in summer.

10. __Borys and Raatz Ph.D. theses completed.__

In May 1983, R. Borys of Colorado State University and W. Raatz of the University of Alaska completed their Ph.D. theses on Arctic air chemistry. Both were sponsored in part by this ONR project. Their results are summarized in Section I.C.

11. __Cooperative program on bromine in the Arctic atmosphere.__

For the past two years, URI and the National Center for Atmospheric Research (NCAR) have had a cooperative program in research on the unusual behavior of bromine in the Arctic atmosphere. It began with discussions between K. Rahn and W. Berg of NCAR, who has been measuring Br in the stratosphere for the last few years. Recently, Dr. Berg has found extremely high concentrations in the stratosphere, unmatched by tropospheric concentrations known anywhere. When K. Rahn told him of the unusually high concentrations of particulate Br in the Arctic atmosphere during spring (discussed in the previous Project Report/Renewal Proposal), he became very interested. The result has been a joint program of further study at Barrow. As part of this program, detailed measurements of particulate and gaseous bromine have been made at Barrow during spring and summer, as well as on the AGASP flights (Section I.B.15) last spring. One paper is about to appear, and another is being prepared. The source for all this Arctic Br is something that has not been encountered elsewhere, and study of it is sure to add significantly to our understanding of atmospheric bromine in general.

12. __URI-USSR project on USSR pollution aerosol.__

For at least three years, we have suspected strongly that the Soviet Union is a source of much or most of the pollution aerosol measured at Barrow, Alaska. Our suspicions were generated originally by our inability to connect more than about half the pulses of pollution aerosol at Barrow with events of flow from Europe. They were reinforced by the noncrustal Mn/V ratio at Barrow, which was found to be too high to have come from sources in western Europe. Once our attention was focused farther east in the Soviet Union, an obvious mechanism of transport was discovered (the so-called Taymyr pathway) which we had overlooked previously.

The big unknown in this equation is the composition of Soviet Union aerosol at the source. At this point we have direct measurements of aerosol from North America as well as western and eastern Europe, but not the Soviet Union. To remedy this, we have been contacting the Soviet Union and proposing a joint study of either the Soviet Arctic or the Soviet source areas themselves. Our first informal approaches were either ignored or turned down. The next approach, through the US-USSR Bilateral Agreement on Protection of the Environment, was for aerosol studies in the Soviet Arctic, and it too was turned down.

In January 1983, a second proposal was made through the Bilateral Agreement, for an elemental tracer study in the Soviet Union. So far, the prospects for its approval seem good. Two Russian scientists visited

URI last April and discussed the proposal in detail. As presently envisioned, the initial study would take place outside Vilnius, Lithuania, and would consist of a straightforward collection of aerosol samples followed by analysis for trace elements and major constituents. From these results, elemental signatures would be sought and developed jointly. If successful, the process would be repeated at other points within the Soviet Union.

The next step is for K. Rahn to pay a return visit to the Soviet Union. This visit is tentatively scheduled for late 1983. The itinerary consists of Leningrad, Moscow and Vilnius.

This project will not be a formal part of our ONR Contract. We have summarized it here because of its relevance and because it illustrates the increasing acceptance of our system of elemental tracers.

13. **K. Rahn to visit PRC; prospects of a joint program on tracers.**

In May 1983, K. Rahn was invited to participate in a delegation of air-quality specialists visiting the People's Republic of China for three weeks in September 1983. The trip is being arranged by People-to-People International, in response to an invitation by the Ministry of Metallurgical Industry of the PRC. The invitation to K. Rahn is a direct result of his activities with elemental tracers and acid-rain problems in the U.S.

While this visit is not a formal part of our ONR Contract, its goals are in harmony with our long-term efforts to develop a system of elemental tracers and apply it broadly. K. Rahn is also in touch with Zhao Dianwu of the Institute of Environmental Chemistry, Academia Sinica, Beijing, who is interested in holding joint discussions on elemental tracers and considering possible cooperative activities. K. Rahn has accepted an invitation to visit Zhao's institute during his trip. He will also meet with his nearest equivalents in China, two researchers who have been using the nuclear reactor at Qinghua University to characterize Beijing aerosols.

14. **Aircraft samples of aerosol from the Eurasian Arctic**

During the last four years, the University of Rhode Island and the U.S. Air Force have engaged in an unofficial joint program whereby aerosol samples taken aloft in the Eurasian Arctic are provided to URI for trace-element analysis. This program was difficult to establish, but now is on a sound footing. For example, we did not know at first whether their samples would be analyzable by neutron activation, because the filter material is impure relative to the ashless cellulose that we use elsewhere Also, the aircraft samples are taken for much shorter periods than we would prefer. But these problems have been worked out, and we now know that we can analyze the samples for enough elements to characterize them reasonably.

Recently, this program was made official. We expect it to continue indefinitely. The information it offers is invaluable.

15.   Participation in AGASP flights

During March and April 1983, four members of our
project (G. Shaw, W. Raatz, R. Borys, K. Rahn) participated in the
NOAA/ONR Arctic Gas- and Aerosol-Sampling Program (AGASP) in the Arctic.
This consisted of approximately 80 hours of research flights in the NOAA
P3 aircraft, based successively in Alaska, Greenland and Norway. These
flights should yield a wealth of information about the third dimension in
the Arctic atmosphere. W. Raatz and R. Borys were present for all three
sets of flights, while G. Shaw and K. Rahn participated in the Alaskan
and Norwegian sections, respectively. G. Shaw took impactor samples. W.
Raatz functioned as meteorologist and observer, R. Borys sampled aerosol,
measured particle-size distributions, and assisted with the
meteorological decisions, and K. Rahn was present as meteorologist and
observer.

A set of approximately 50 high-volume aerosol samples from the
flights is now being analyzed at the University of Rhode Island.

16.   Cooperative program with NILU/BP

URI and the Norwegian Institute for Air Research
(NILU) have cooperated on studies of the Norwegian Arctic for many
years. Recently, B. Ottar and NILU have received a large contract from
British Petroleum for study of the Norwegian Arctic, and have offered URI
the chance to analyze their high-volume aerosol samples. URI is happy to
participate in the BP project, because it offers the most detailed look
at air quality in the Norwegian Arctic ever. URI has just received its
first set of filters from NILU, from their intensive spring campaign of
March-April 1983. It consists of over 100 samples from 9 collection
sites. Samples from subsequent campaigns will be sent to URI when
available.

17.   Diffusion battery/particle counter constructed.

In order to measure the particle-size distribution of Arctic
aerosol throughout the Aitken range (which will give an idea of particle
dynamics in the Arctic), a diffusion battery was constructed at the
University of Alaska. This device incorporated polycarbonate diffusion
screens with monodisperse pores ranging in diameter from 0.6 to 8 μm.
Sixteen different size ranges of aerosol could be counted by using
different pore sizes and flow rates.
The particles were counted with a photoelectric condensation-
nucleus counter similar to a Nolan-Pollak counter, which was also built
at the University of Alaska. This instrument was calibrated against the
Nolan-Pollak counter at the GMCC station in Barrow.

18.   Optical measurements in Fairbanks and Barrow.

Our traditional optical measurements continued in
Fairbanks and Barrow. Seasonal variations of optical depth at the two
sites were recently reported by G. Shaw in the Journal of Applied
Meteorology.

19.   Single-particle analysis of Arctic aerosol

Using a scanning electron microscope and electron
microprobe, the University of Alaska has measured a variety of trace
elements in individual aerosol particles from the Alaskan and Norwegian
Arctic, as well as Antarctica. The results were recently published in
Atmospheric Environment, and are discussed in Section I.C. below.

20.   Photo-reactivity of air near Fairbanks.

The University of Alaska is presently studying the
photo-reactivity of Alaskan air masses near Fairbanks. Filtered air from
Ester Dome outside Fairbanks was irradiated with ultraviolet light, and
the results were related to the different air masses found there. This
project is discussed in Section I.C. below.

21.   Ptarmigan record examined.

Arctic haze was first discovered during the Ptarmigan
weather-reconnaissance missions over the Alaskan Arctic which extended
from the late 1940's through the mid-1960's. In an effort to glean
whatever historical information might be present in these records, W.
Raatz of the University of Alaska has gone through the microfilmed
observer sheets and extracted all observations concerning haze. The
results are most interesting, although incomplete, and form part of his
Ph.D. thesis.

C.   Results

1.   The four-year record of trace elements in the Barrow
aerosol.

We have analyzed the first four years of filter
samples from Barrow for sulfate by turbidimetry and for trace elements by
short-lived neutron activation. For all constituents with good
analytical results, well-defined and reproducible seasonal variations
were found. Figures 1 and 2 show the results for seven constituents.

Figure 1 shows the four-year monthly means for the naturally
produced elements Al (from soil), Na (from the sea) and non-seasalt Br.
Al had a sharp peak in July, which was probably related to dry open
ground near Barrow. Other than that, only a broad, gentle winter maximum
was seen. Na peaked during the stormy fall and fell off strongly during
the quieter late spring and early summer. Non-seasalt Br had a very
strong peak during March and April (see Section I.C.11 for further discus-
sion of Br).

Figure 2 shows the record for four pollution-derived elements.
Elemental C had a pronounced November-December peak in addition to a
spring maximum. Noncrustal Mn had a fall plateau followed by a spring
maximum.   Noncrustal V and nonmarine sulfate each had smaller fall
concentrations relative to their very large spring maxima.

Thus, pollution aerosol at Barrow seems to receive a fall pulse
from sources rich in C and Mn, followed by a stronger and longer spring

BARROW ALASKA, 1976-81-MONTHLY MEAN

AL (NG/SCM) VS MONTH (1=SEPT)
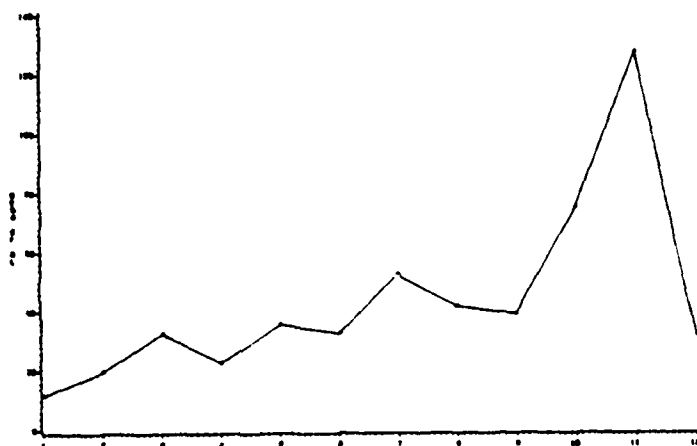
BARROW ALASKA, 1976-81-MONTHLY MEAN

NA (NG/SCM) VS MONTH (1=SEPT)
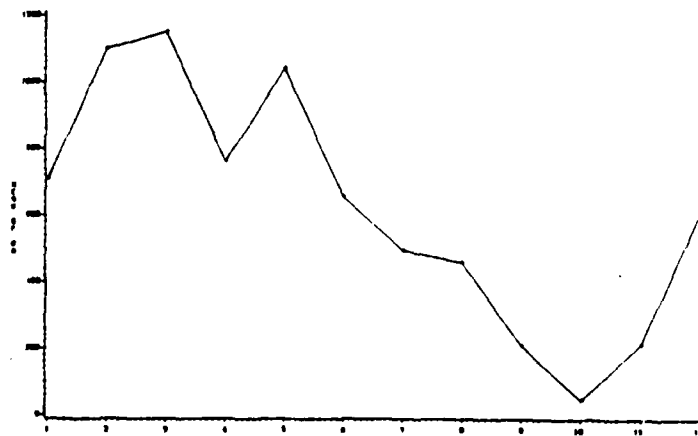
BARROW ALASKA, 1976-81-MONTHLY MEAN

XBR (NG/SCM) VS MONTH (1=SEPT)

Figure 1.   Four-year monthly averages of Al (from soil), Na (from
the sea) and nonmarine Br in the Barrow aerosol.
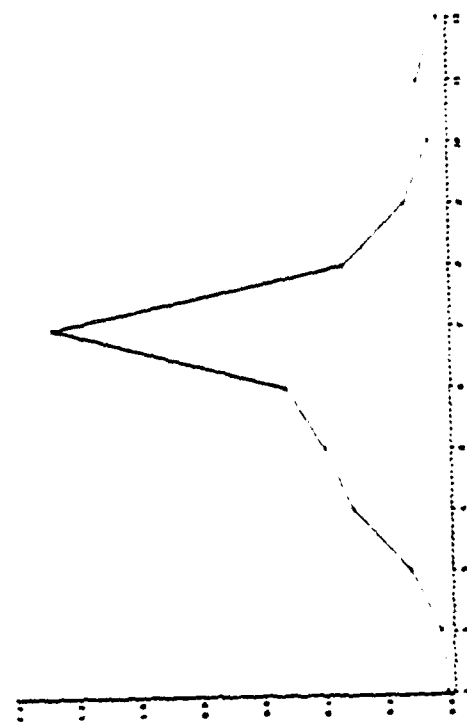
Figure 2. Four-year monthly averages of the pollution-derived elemental C, noncrustal Mn, noncrustal V, and nonmarine sulfate in the Barrow aerosol.

maximum from sources rich in V. We believe that the fall aerosol comes mostly from the Soviet Union, whereas the spring aerosol comes more from Europe.

2. SO_2 at Bear Island

K. Rahn of URI spent three months of summer 1979 at the Norwegian Institute for Air Research. One of the results of this visit was a joint article on SO_2 at Bear Island published in __Nature__ (reproduced as Section I.E.3 here). The main conclusions of this study were that SO_2 in the Norwegian Arctic is highly pulsed during winter (like aerosol), and that the majority of the pulses (10 of 13 for winter 1978-79) came via "return-flow" cyclonically curved pathways (in which air from the south enters the Norwegian Arctic from the E-NE), rather than directly from the south as might have been expected. This observation showed just how important the Icelandic low-pressure area is as a determiner of air quality in the Arctic. (Later, a more easterly variant of this path came to be recognized as the principal explanation for haze at Barrow.)

The importance of the return-flow pathway also focused attention on potential sources of aerosol farther east, i.e., in eastern Europe and the western Soviet Union. Subsequent work has confirmed the importance of these sources for the Norwegian Arctic.

3. Eurasia as a source of Arctic haze

Since about 1978-79, we have become increasingly convinced that the principal sources of Arctic haze lie in Eurasia, not North America. The reasons for this have been partly meteorological, partly chemical. In one of the articles from the 1980 Second Symposium on Arctic Air Chemistry (Rahn, "Relative importances of North America and Eurasia as sources of Arctic aerosol", Section I.D), we listed all the arguments pro and con in detail. While no single argument could be considered proof-positive, they were quite impressive and convincing when taken collectively. As detailed in the next two sections, they have been supported by increasingly sophisticated chemical evidence. We and others now believe that the bulk of Arctic aerosol comes from Eurasian sources. Although there may be occasional events from North America, none has been clearly demonstrated to date.

4. The noncrustal Mn/V ratio: first regional tracer of pollution aerosol.

In spite of all the meteorological and observational arguments offered for the Eurasian source of Arctic haze, we felt that a more direct form of evidence on its origins was needed. For some time, we had believed that the chemical composition of the aerosol itself was most likely to contain the answers, via its detailed elemental composition. We reasoned that if enough elements could be involved, systematic differences between at least some of them in some source areas were sure to emerge.

The first success came in 1980, with the noncrustal Mn/V ratio. Until then, we had sought elemental tracers via aerosol-crust enrichment

factors. Our new approach was to discard the crustal fraction of the aerosol altogether and work exclusively with ratios of pollution-derived elements. The noncrustal Mn/V ratio was the first of these, and was intended specifically to discriminate between eastern North America and western Europe. It did this quite satisfactorily (ratios in the two areas differed by a factor of five), and showed that (a) contributions from North America to Arctic aerosol were probably minor, and (b) Barrow had higher ratios than the Norwegian Arctic did and hence had sources with less western European character. The Mn/V ratio was first described in the August 1981 issue of Atmospheric Environment.

On balance, the Mn/V ratio was a complete success. We have felt for some time, though, that its specific successes were less important than the basic fact that it worked, and hence demonstrated that elemental tracers of source areas could be found. We have often referred to it as the "great icebreaker".

5. New, more powerful seven-element tracer system.

Our major accomplishment of the last three years is the development of a seven-element system of regional tracers. We have put an enormous amount of effort into this task, because we judged it to be so important to so many areas of atmospheric science. Virtually every piece of trace-element data we ever generated has gone into this system. The system and several applications are explained in the Rahn-Lowenthal article submitted to Science and given here as Section I.E.5. Using selected elements and the appropriate statistical techniques, we have been able to show that: (a) at least seven well-defined regional signatures of pollution aerosol are discernable in North America and Europe; (b) as expressed by six elemental ratios to Se, these signatures are all different; (c) a small number of elements contain the majority of the tracer power; without them, regional aerosols cannot be discriminated; (d) regional signatures can be followed during transport of up to several thousand km; (e) the contributions of various regions to mixed aerosols can be apportioned element by element; (f) provided that the aerosols are reasonably well aged, regional contributions to secondary constituents like sulfate can be determined; (g) the system confirms the Eurasian origin of Arctic aerosols.

Our tracer system can also be used with certain strong point sources of aerosol. To date, we have worked with signatures of three nonferrous smelters or complexes (New Jersey Zinc, the Sudbury Basin, Noril'sk) and are beginning on a fourth (Nikel'). We have also been able to show that one particularly strong pollution episode in Scandinavia came from eastern Europe, not western Europe. In North America, we have demonstrated the importance of coastal sources on coastal sites and interior sources on interior sites. We have found a new and unsuspected signature of New England/Eastern Canada aerosol which can be used to differentiate northern air from southern air in New England. In the Arctic, we have detected the Noril'sk plume at Barrow.

We now believe that the future of elemental tracers is extremely bright. In the coming years, our most important task will be to develop this field as far and as fast as we can. Nearly all our work will

involve elemental tracers in one form or another. We rank the discovery and development of elemental tracers with our work on Arctic haze and long-range transport.

6. **Particle-size distributions of the Barrow aerosol (Lewis M.S. thesis, URI).**

Ms. Noëlle F. Lewis of URI is finishing her M.S. thesis on particle-size distributions of trace elements in the Barrow aerosol. This topic was selected because little was known about the preferred particle sizes of trace elements in the Arctic compared to their total concentrations. We felt that it was important to know whether the extreme aging of the Arctic aerosol had mixed all elements onto the same sizes or whether they retained their original differences. The more the size distributions at Barrow resembled those in the Eurasian source regions, the more directly our elemental tracers could be applied to the Arctic aerosol.

Ms. Lewis has been analyzing cascade-impactor samples of aerosol from both Barrow and selected European source regions. The answers are straightforward: the Barrow aerosol is surprisingly similar to its precursors. Small-particle elements in Europe are small-particle at Barrow, large-particle elements in Europe are large-particle at Barrow. During the spring maximum of Arctic haze, the fine-particle mode at Barrow is enriched relative to the large particle mode in other seasons. This agrees with particle measurements made by G. Shaw in Fairbanks.

These results mean that we can apply Eurasian signatures to Arctic aerosol with much less risk than we might have feared otherwise.

7. **Sources of pollution aerosol in eastern North America.**

One of the most important applications of our new seven-element tracer system so far has been to the problem of origins of acid rain in eastern North America. The United States is now poised to reduce its emission of SO_2 in the East. Depending on the approach chosen, costs may be as much as $2-10 billion per year for 10 years. Thus, a mistake could prove extremely costly. We have come to believe that the sources of acidity in eastern North America are not known with any precision, especially for a given air mass or a given rain, in spite of all the modelling that has been done. But elemental tracers should offer the kind of resolution that is needed, i.e., they should be able to discriminate between northeastern and midwestern sources, for example. As a result, we have been racing to determine the sources of acidity before decisions on controls are reached, which may well come by the end of 1983. We are very close to a preliminary answer, and expect to know it within a month or so as well as we will for the next year. It would be presumptuous to say that only we have the answer. But elemental tracers do offer a directness of discrimination that is impossible otherwise. For the near future, we can think of no more important application of elemental tracers than this.

The _Science_ preprint (Section I.E.5) gives our current ideas about the sources of aerosol in eastern North America.

8.   Noril'sk aerosol at Barrow

One of N. Lewis' six cascade-impactor samples from Barrow had a highly anomalous trace-element pattern, with greatly enriched As, In and Sb. The pattern of ratios to Se seemed to match that of the Noril'sk smelting complex, as determined from the aircraft samples in the Eurasian Arctic described in Section 11 below. None of the 50 other samples from Barrow had this signature. A check of the meteorological maps revealed that Noril'sk was indeed the likely source, for the days preceding this sample were marked by very strong flow from Noril'sk directly northward deep into the Arctic. It is roughly 4000 km from Noril'sk to Barrow. To the best of our knowledge, no point source of pollution aerosol has ever been tracked this far before, especially at ground level.

One interesting aspect of our results was that the sulfate content of the air at Barrow was no higher with the Noril'sk signal than without it. This suggests that Noril'sk, even though it is a very strong point source, is not a major source of Arctic aerosol in general. We have found a similar result for the Canadian smelters and aerosol of the Northeast.

We have submitted an article on these findings to Nature.

9.   Black and white episodes as precursors to
Arctic aerosol.

From the beginning of our work at Barrow, we have been impressed by the large amount of sulfate in the pollution aerosol of winter compared to that expected from the abundances of other trace elements. The first indication of this came in 1978 when we could not account for the degree of haze based on vanadium as an indicator of pollution, but could account for it after we measured sulfate and found ten times more than predicted. The most logical ·xplanation for all this sulfate was unusually great aging of polluted air, during which SO_2 is progressively converted to particulate sulfate. Subsequent data from Scandinavia, where an intermediate value of sulfate was found relative to vanadium and selenium, reinforced our suspicions.

In 1976 and 1978, Professor C. Brosset of Gothenburg, Sweden published two papers describing what he termed "black" and "white" pollution episodes in Scandinavia. In each, the amount of sulfate aerosol was large, but aerosol of black episodes had much more black carbon than did white episodes. Although the pollution in both types of episodes originated in central Europe, Prof. Brosset's articles dwelt on the divergent characteristics of black vs. white episodes. We, however, saw black and white episodes in quite a different light, as intermediate stages of a general process of atmospheric aging which eventually led to the Arctic aerosol.

The first clue to this new interpretation came from the parallel behavior of the sulfate/carbon ratio in Brosset's episodes and the sulfate/vanadium or sulfate/selenium ratio in the Arctic. As an air mass ages, the ratio of sulfate to primary constituents such as carbon, vanadium and selenium should increase. In Brosset's case, the ratios

were higher in white episodes (European air coming to Scandinavia via a roundabout pathway over the Atlantic) than in black episodes (direct transport from central Europe northward). In other words, white episodes were more aged than black episodes. In our case, similar differences in ratio were observed between European source areas and the (aged) Arctic.

In cooperation with Prof. Brosset, we combined data on black and white episodes with our data from Europe and the Arctic to show that they all fit together into a consistent picture of progressive atmospheric aging of air masses (Figure 3). The results were presented at the General Motors Symposium on particulate carbon, and were published in the proceedings. In our view, much of the mystery of black and white episodes has now been removed.

10. Cloud-active aerosol in the Arctic

Cloud-active aerosol in the Arctic was the subject of the Ph.D. thesis of R.D. Borys of Colorado State University, which was completed in May 1983. Specifically, Dr. Borys wished to investigate whether the large amounts of pollution aerosol which are transported to the Arctic each winter affected the nucleation of water there. He suspected that it might, because sulfate, the major constituent of the Arctic aerosol, is a very important cloud-condensation nucleus in midlatitudes, and soil particles, which are also transported to the Arctic, are good ice nuclei.

Dr. Borys measured the activities of cloud-condensation nuclei and ice nuclei at several sites in the Arctic in both summer and winter. His results showed clearly that cloud-condensation nuclei varied nearly directly with sulfate (i.e., were much higher in winter than in summer), but that concentrations of ice nuclei varied oppositely. The reason for the latter behavior is not clear. It may be from quenching of the soil particles by a coating of dilute sulfuric acid, or alternatively from removal of the ice nuclei by snowout before the air mass reached the Arctic. Whatever the explanation for ice nuclei, there seems little doubt that cloud-condensation nuclei in the Arctic are affected by pollution aerosol.

The abstract of Dr. Borys thesis is reproduced here as Section I.E.1.

11. World-record bromine concentrations at Barrow in spring.

For some years now, we have observed a regular springtime maximum in bromine in our filters from Barrow (Figure 4). Because of the sharpness of this peak and the height of the concentrations reached, we felt that the bromine could not have been pollution-derived.

We have discussed this phenomenon with Dr. Walter Berg of the National Center for Atmospheric Research, and are now investigating Arctic bromine jointly with him. He has measured gaseous bromine at Barrow during the spring maximum. In fact, the bromine concentrations in the Arctic troposphere during spring (nearly 500 ng m^{-3}) are the
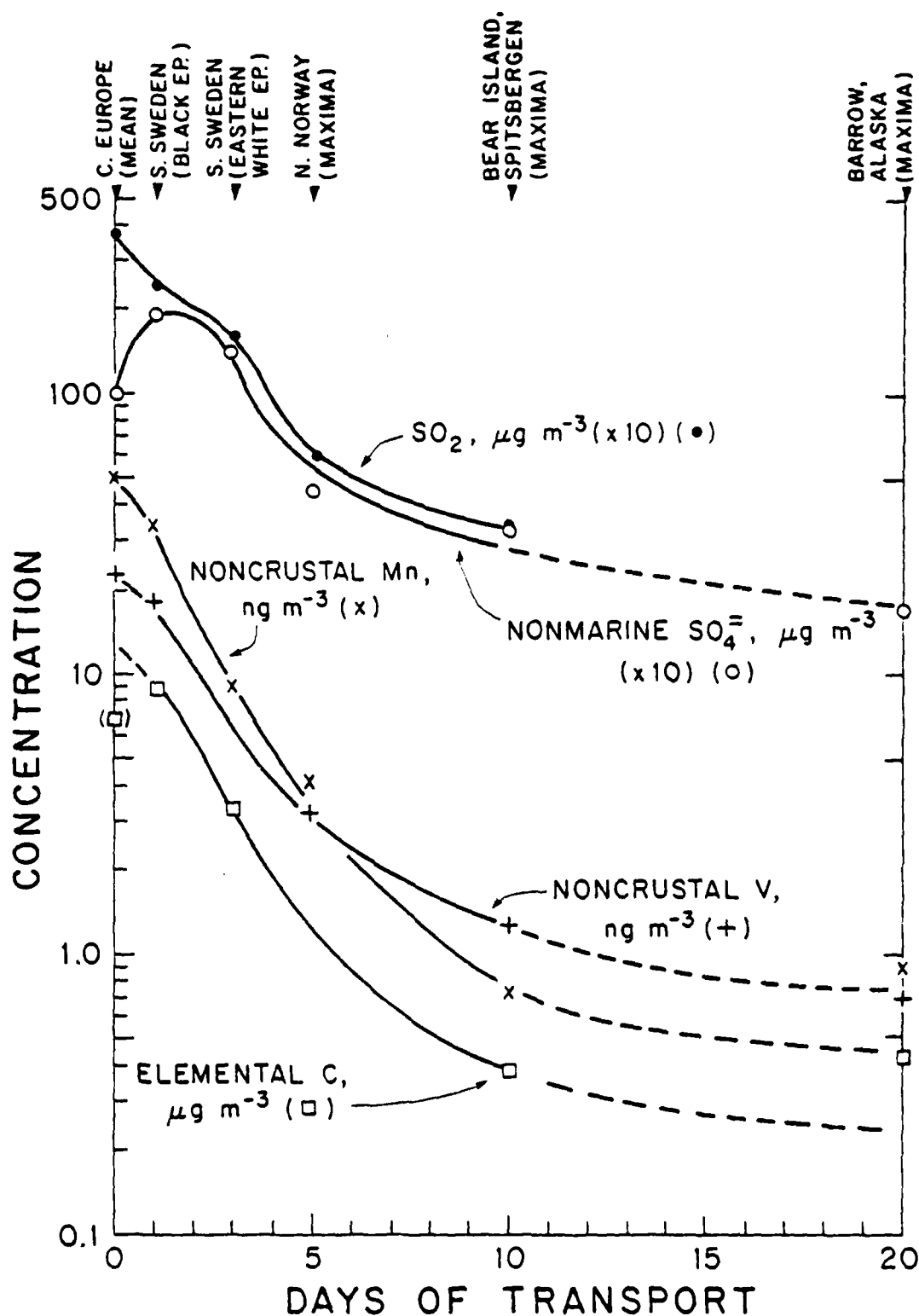
Figure 3. An aging diagram for aerosol in Europe, Scandinavia, and the Arctic.

FOUR YEARS OF PARTICULATE BROMINE DATA FROM PT. BARROW, ALASKA 1976 to 1979
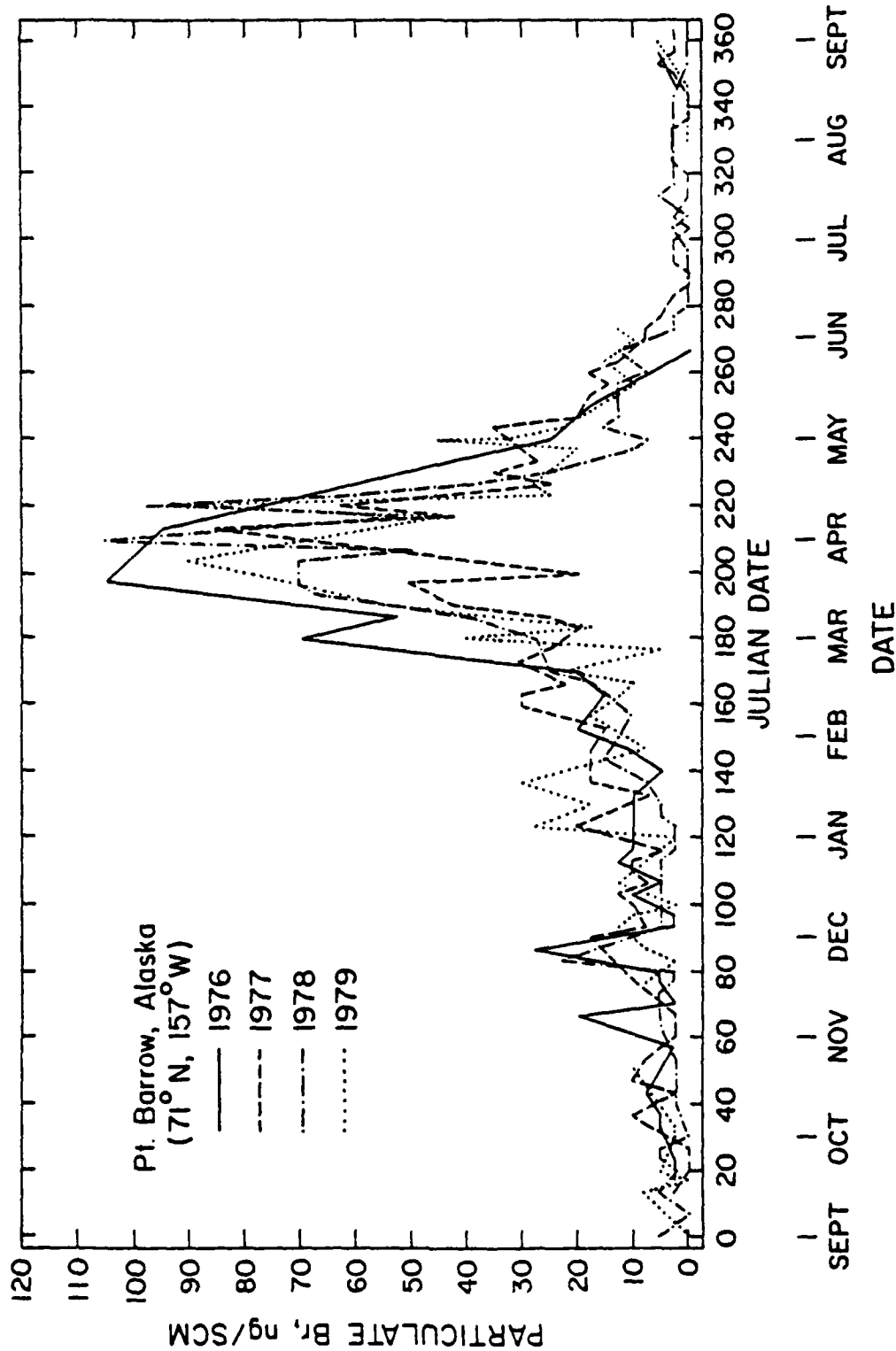
Figure 4.

highest found anywhere in the world. It is truly a bizzare occurrence
for which we have no explanation at present.

The cooperative study is continuing. NCAR will be examining the
speciation of gaseous bromine in detail. Hopefully, similar experiments
can be conducted at other sites in the Arctic to investigate the
generality of the phenomenon. Eventually, the Antarctic will be studied
as well.

The significance of Arctic bromine is at least twofold. First,
the Arctic is clearly a strong natural source of bromine that was not
recognized previously. The Arctic Ocean is likely to be the source, but
it is not yet known whether the bromine is released physically or
biologically. Second, Dr. Berg has recently measured extremely high
concentrations of bromine in the lower stratosphere. Until the Arctic
data were available, he had no idea what the tropospheric source might
have been. Although the Arctic is by no means proven to be the source,
it is presently the only reasonable candidate. Stratospheric bromine is
of great interest because of its potential role in the ozone cycle. Per
unit mass, bromine is a much more efficient catalyst for destroying ozone
than chlorine is.

12. Aerosol in the Eurasian Arctic.

Our cooperative program with the Air Force on analy-
sis of aircraft samples of aerosol from the Eurasian Arctic has yielded
several results of significance. First, we have determined that the
samples can be analyzed for typically 30 elements, at least during
winter. Of these, roughly six are contaminated; the rest are available
for tracer purposes. Second, at least four characteristic elemental
signatures have emerged from the analyses. They correspond roughly to
the central Soviet Union, the Noril'sk smelting complex, Europe, and
Arctic background pollution. Third, concentrations are usually higher
than at Barrow. Fourth, ground-level aerosol at Barrow during fall and
early winter matches that from the Soviet Union quite closely, whereas
during spring it often appears to be more European. Fifth, the Noril'sk
signature matched one set of observations from Barrow. Sixth, the compo-
sition of aerosol in the Eurasian Arctic is often quite heterogeneous
over small distances. Seventh, there is elemental information (signa-
tures) in these results which we have not yet been able to interpret
fully.

13. Eddy-diffusion transport to the Arctic?

In 1981, G. Shaw of the University of Alaska published
a paper in the Arctic isssue of Atmospheric Environment (see Section
I.D.) in which he proposed that the aerosol loading of the Arctic could
be reproduced to within a factor of two by eddy-diffusion considerations
alone. The implications of this were that organized transport from
midlatitudes to the Arctic might not dominate diffusive transport. This
idea was highly controversial. In the last two years, the meteorological
analysis of W. Raatz and the detailed chemical studies at the University
of Rhode Island have both produced new information which is most
interpretable in terms of organized transport. Raatz was able to link
individual pollution episodes at Barrow with prominent synoptic features

which favored organized transport. He was also able to correlate the
seasonal cycle of the noncrustal Mn/V ratio at Barrow with the westward
migration of these features across Eurasia during winter. The URI
studies showed that different kinds of pollution aerosol were found at
Barrow, each corresponding to specific source regions within Eurasia.
More recently, URI data from the Eurasian Arctic showed heterogeneities
incompatible with extensive eddy diffusion. Thus it would appear that,
while eddy diffusion certainly tends to smear out aerosol during
long-range transport to the Arctic, it probably does not equal or exceed
the effects of organized transport. One must think in terms of organized
transport modified somewhat by diffusion, not the reverse.

14. Springtime maximum in turbidity near Fairbanks.

One of the earliest results of our aerosol sampling
near Fairbanks revealed strong pulses of pollution aerosol from the
Arctic during spring. Now that more optical data are available from
Fairbanks, Dr. Shaw has confirmed that these invasions of aerosol also
create a springtime maximum in haze there. This is in marked contrast to
the rest of the winter outside Fairbanks, when the atmosphere is
extremely low in turbidity.

15. Single-particle analysis of Arctic aerosol.

Dr. Shaw has also used a scanning electron
microscope/electron microprobe to measure the abundances of several
elements in single aerosol particles from interior Alaska and Kungsøya.
The results from both sites showed that the coarse fraction of the
aerosol was composed mainly of sea salt and soil dust, occasionally
coated with a sulfurous layer, whereas the fine-particle fraction was
predominantly sulfurous. Other interesting elements such as Cu were
found occasionally, but their data were too few to draw any conclusion
concerning their sources. The most important result of this study was
that sulfur seemed ubiquitous in the Arctic atmosphere.

16. Particle-size distributions of Arctic aerosol

Dr. Shaw has used his home-built diffusion battery/
nucleus counter system to measure the particle-size distributions of
aerosol of interior Alaska. In general, he found that aerosol during
nonhaze periods (from the Pacific) was unimodal, with a particle maximum
near radius 0.01 μm, and relatively high particle counts (300-2000
cm^{-3}). In Arctic haze, however, the particles were bimodal, with
maxima near radii 0.003 and 0.05 μm, but had twofold lower particle
counts. Most significantly, though, haze aerosol had twofold greater
mass loading near radius 0.1 μm.

17. Photo-reactivity of air near Fairbanks

In a series of experiments with filtered air from the
Ester Dome Observatory outside Fairbanks, Dr. Shaw has shown that air
from the Pacific produced large numbers of tiny particles when irradiated
with ultraviolet light, whereas air from the Arctic produced none.
Addition of NO_x and H_2S to nonreacting air still produced no
particles. SO_2, NH_3, and SO_2 plus NH_3 all produced particles

upon irradiation, the latter giving rise to large blue particles. HNO_3 produced particles even before irradiation. Based on these results, Dr. Shaw concluded that the production of nuclei in nonhaze air near Alaska probably involves NH_3.

18. Meteorological aspects of Arctic haze

In May 1983, Dr. W. Raatz of the University of Alaska completed his Ph.D thesis on the meteorological aspects of Arctic haze. The principal result of this thesis was its success in relating the occurrence of the haze and its composition to synoptic features in Eurasia and the Arctic. According to Raatz, the major transport of pollution aerosol occurs when Arctic and midlatitude pressure systems remain stable for several days. He also concluded that the zone best suited for transporting aerosol was on the periphery of quasi-stationary anticyclones where the pressure gradients are strong. The seasonal variation in Arctic aerosol was explained mainly by the corresponding variations of midlatitude blocking anticyclones, of the Arctic anticyclone, and of the Asiatic anticyclone. The intensification and westward migration of the Asiatic anticylone during winter and spring is responsible for the dominance of central Soviet Union aerosol at Barrow early in the winter followed by a shift toward European character in spring.

Lastly, Dr. Raatz showed that the chemical characteristics of air masses moving to Barrow are retained longer than their meteorological characteristics are. In our view, this is one of the strongest possible arguments in favor of developing a system of elemental tracers for use in the atmosphere.

The abstract of Dr. Raatz's thesis is reproduced here as Section I.E.2.

19. "Ptarmigan" records of Arctic haze

As part of his Ph.D thesis research, Dr. Raatz also examined the original records from the "Ptarmigan" missions. According to these records, most of which came from the early 1950's, the maximum frequency of visual haze was in spring (the same time that modern pollution aerosol is at a maximum near Barrow). Interestingly, Raatz was able to show that haze during the Ptarmigan missions was a result of the same types of circulation from the Soviet Union and Europe as is found for pollution aerosol today. Lastly, Raatz produced evidence for a desert-dust component of haze during summer.

D. Publications resulting at least in part from this project,
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E. REPRINTS OF SELECTED PUBLICATIONS

E.1. Abstract of Ph.D. thesis of R.D. Borys, Colorado State University,
      May 1983.

ABSTRACT OF THESIS

THE EFFECTS OF LONG-RANGE TRANSPORT
OF AIR POLLUTANTS ON ARCTIC CLOUD-ACTIVE AEROSOL

Arctic Haze, observed over much of the Arctic during winter,
consists of submicron primary and secondary pollutant aerosol particles
transported from mid-latitude source regions. These pollutants, if
present would alter the concentration of cloud-active aerosols. Cloud-
active aerosol particles are responsible for the heterogeneous
nucleation of water (cloud condensation nuclei, CCN) and ice (ice
nuclei, IN) in the atmosphere and are responsible for the initial
microphysical structure of clouds. Cloud microstructure determines, in
part, the radiative properties and colloidal stability of a cloud. A
change in the climatically important cloud-active aerosol particle
concentration over an extended period would alter the radiation balance,
leading to a change in temperature. This would change the pole to
equator temperature gradient which is the driving force of the
atmospheric general circulation.

A series of studies was conducted at several arctic locations to
determine the relationship between CCN and IN and the pollutant aerosol.
The trace elemental composition of the total aerosol was used to
determine when anthropogenic aerosol was present. Variations of the
elemental composition of the aerosol and concentrations of the cloud-
active aerosol particles were compared. The arctic sites were chosen to
lie along proposed pollutant aerosol transport paths to the Arctic.

Various comparisons between pollutants and cloud active aerosols have been made on a day by day basis and for summer and winter seasons. The differences between the nucleational properties of Arctic Haze aerosol, which is pollution derived, and the natural background aerosol of the Arctic have been determined.. The elemental composition of the aerosols, combined with meteorological analysis, have been used to assess the relative importance of the pathways.

Results show the CCN concentrations are positively correlated with the pollutant aerosol concentration on both a daily and seasonal basis. Concentrations of IN were found to be lowest during the winter when pollutant aerosol was present. Day-to-day variations of IN were related to both natural and pollutant aerosol sources depending upon the location and season. The lower IN concentrations which occurred during winter when pollutant aerosol concentrations were at a maximum may be a result of preferential removal of IN in the cold Arctic atmosphere or a 'poisoning' of the nuclei by the pollutants. Interpretation of the results provides evidence that pollutant aerosol transport from Eurasia directly to the north is primarily responsible for Arctic Haze.

The effects of pollutant transport to the Arctic on cloud microstructure may be significant. If the results of the surface-based cloud-active aerosol measurements can be extrapolated to arctic clouds, and if homogeneous ice nucleation is not a major determinant for Arctic cloud ice crystal concetrations, clouds which form in the polluted arctic airmass might have fewer ice crystals and more cloud drops per unit volume of cloud. The resulting clouds would be more colloidally

stable and optically thick than clouds which would have formed had no

pollutants been present.

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Spring, 1983

E.2. Abstract of Ph.D. Thesis of W.E. Raatz, University of Alaska, May 1983.

ABSTRACT

A time series of concentrations of pollution aerosols collected over a period of four years in the near-surface air at Barrow, Alaska, was used to investigate tropospheric long-range transport of anthropogenic pollution from mid-latitudes into the Arctic. This transport takes place when the mid-latitudinal and arctic atmospheric circulations remain in a quasi-persistent mode. Sudden changes in the circulation pattern explain the episodic character of the arctic pollution aerosol. Transport of aerosols is accomplished by quasi-stationary anticyclones and takes place along their peripheries where pressure gradients are relatively strong. The seasonal variation in concentration of the arctic pollution aerosol is explained by the seasonal variation in the occurrence and position of mid-latitude blocking anticyclones, of the arctic anticyclone, and of the Asiatic anticyclone. The positions of the major anticyclonic centers are responsible for the fact that Soviet industrial sources contribute to the arctic pollution aerosol predominantly during winter, European sources during spring, and that North American and Far Eastern industrial sources contribute little to the arctic pollution aerosols.

Air masses carrying pollutants can be traced by their chemical characteristics obtained over the source regions, however, the original meteorological characteristics are lost during the transport which lasts for about 8-9 days.

A second data set, collected during the "Ptarmigan" weather reconnaissance flights, was investigated for observations of Arctic Haze over the Alaskan Arctic. A connection between Arctic Haze and the arctic pollution aerosols is suggested, for the occurrence of Arctic Haze undergoes a similar seasonal variation as that of the pollution aerosols, and similar circulation modes leading to the Soviet Union and Europe can be found during the presence of Arctic Haze. In addition, the data seem to suggest that besides a probable pollution-derived component during winter/spring Arctic Haze might be desert dust-derived during summer.

E.3.

High winter concentrations of SO₂ in the Norwegian Arctic and transport from Eurasia

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Since July 1977, the Norwegian Institute for Air Research has been studying trace gases and aerosols in the atmosphere at Bear Island, an Arctic site located at 74° N and 19° E. Although Bear Island lies well north of the Arctic Circle, the warm Norwegian Sea gives it an annual mean temperature of −1.8 °C, considerably warmer than at many other Arctic locations (Barrow, Alaska, for example, is 350 km farther south but has an annual mean of −12.2 °C). In summer, Bear Island is surrounded by open water; in winter there is open sea to the south and west and pack ice to the north and east. Atmospheric samples are taken 20 m above mean sea level and 2 m above local ground: high-volume filters are taken three times a week and analysed for various elements by atomic absorption, neutron activation and wet chemistry; sulphate and sulphur dioxide are measured daily by a method similar to that of Johnson and Atkins[1], using low-volume (16 m³) prefilters for sulphate and KOH-impregnated afterfilters for SO₂. The collection efficiency of this method has been tested extensively[2]. Results for the high-volume samples have been reported[3]; here we discuss the SO₂ data, which seem to indicate that during winter there is efficient transport from Eurasian midlatitudes, due at least in part to long atmospheric residence times in and around the Arctic.

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During summer, Bear Island has a narrow temperature range (typically 0–10 °C at noon) and persistently low concentrations of SO₂ (at or below the detection limit of 0.2 μg m⁻³). For example, from May to October 1978 there were only 10 days with SO₂ concentrations > 0.4 μg m⁻³. During winter, however, the weather becomes more variable (temperatures range from 0 to −30 °C); SO₂ concentrations (and those of aerosol) often become much higher. For example, from November 1977 to April 1978 there were 65 days with SO₂ concentrations > 0.4 μg m⁻³. Concentrations of SO₂ are also highly episodic in winter, with about three to five irregularly spaced pulses per month. Pulse duration can vary from one day to more than a week. Between pulses, SO₂ concentrations are at the summer values, whereas daily mean concentrations in pulses reach 1–6 μg m⁻³. Figure 1 records SO₂ concentrations from mid-December 1977 to mid-April 1978. c indicates probable contamination by the local diesel generator, deduced from wind observations every three hours.

Three of these pulses were associated with warm air from the south (0 to −5 °C), but 10 were associated with colder air (−10 to −30 °C). Wind direction during the cold-air episodes was typically northeastern at the surface and N–NE at 1,500-m elevation (which eliminated the possibility of local contamination from the north-west causing the high SO₂ values). wind speed was often high (>10 m s⁻¹) during cold-air episodes. During the period of Fig. 1, nearly every pulse of cold air at Bear Island had high SO₂ concentrations.

There is considerable evidence that this 'Arctic' SO₂ is derived from distant pollution sources, probably the Eurasian midlatitudes. (1) There is no correlation between the presence or elevation of local temperature inversions and SO₂ (or aerosol) concentrations, as would be expected if local sources dominated. With E–NE winds, there may be either ground-based temperature inversions or near-adiabatic profiles to a few hundred metres with an inversion above that. With W–SW winds there are usually surface-based inversions. (2) Aerosol species such as sulphate, vanadium and lead usually peak at the same time as SO₂, and have high enough concentrations (2–4 μg m⁻³, 1–3 ng m⁻³ and 5–10 ng m⁻³, respectively) to suggest that they have come directly from polluted areas. Of these, at least
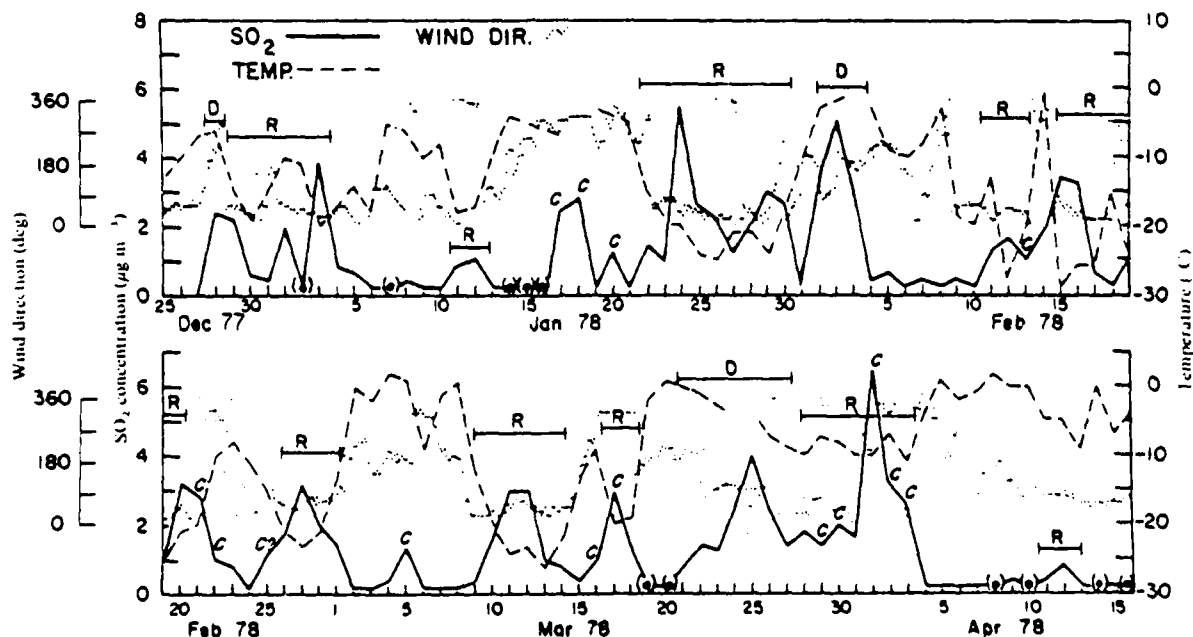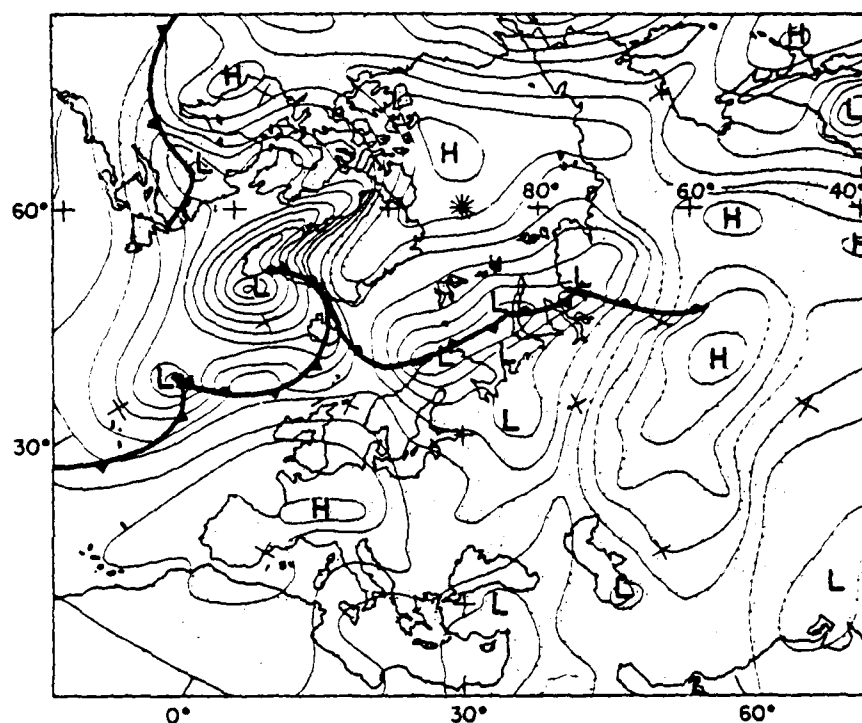

Fig. 1 Daily SO₂, temperature and wind direction at Bear Island. December 1977 to April 1978. D, Direct flow: R, return flow; c, probable contamination by local diesel generator.

Fig. 2 Simplified surface synoptic situation for 10 March 1978, typical for cold-air episodes of SO_2 at Bear Island. H, High pressure; L, low pressure.

vanadium has its main pollution sources in midlatitudes[4]. Occasionally, however, peaks of aerosol are not accompanied by peaks of SO_2. (3) Preliminary trajectory analysis indicates that during cold-air episodes, air flows to Bear Island around the eastward and northward sides of one or more low-pressure centres located over or just north of Scandinavia and the western USSR. A typical surface synoptic situation, for 10 March 1978, is shown in simplified form in Fig. 2. Surface-geostrophical five-day back-trajectories (which represent air flow between the surface and 1,500 m) for five high-SO_2, cold-air days at Bear Island during winter-spring 1978 are shown in Fig. 3. These trajectories, which are only rough guides to how the air masses could have travelled, indicate that for four of the five days, the air reaching Bear Island did seem to curve cyclonically around the low-pressure system, coming first from the region between Novaya Zemlya and the Taymyr Peninsula, and before that from farther south in the western USSR. Allowing for large-scale lateral diffusion, many of the densely populated areas of the western USSR and Europe are included within travel times of roughly 5-10 days. We call this the 'return-flow' pathway from Eurasia to the Norwegian Arctic.

A similar pathway to the Arctic was proposed earlier[4] for aerosol. The return-flow pathway is different from the 'direct-flow' pathway, where air flows northward from Europe to Bear Island, on the eastward side of a low-pressure centre located more to the south or west, and creates a warm-air episode[1]. In Fig. 1, these two types of air flow, as determined from surface meteorological maps, are indicated by 'R' and 'D', respectively.

The reason for the different character of the trajectory of 24 January 1978, which apparently came from the north, is not clear. The general synoptic situation at that time was similar to those for the other four cases of high SO_2, consequently, we think that the high SO_2 of 24 January came ultimately from the south as well. This illustrates the uncertainties of meteorological analysis in the Arctic, where weather stations are spaced widely.

The five trajectories for days of low SO_2 came from other directions. Three originated north and east of Bear Island, one came from North America via the North Atlantic, and one even

came from Scandinavia and Europe. The trajectory of 6 February, which seemed to bring very low SO_2 from Europe, is another problem. It came a few days after a strong direct episode, but with considerably weakened pressure systems by the time it had reached northern Norway. Aerosol concentrations were still one-third to one-half of their values at the peak of the episode, but for some reason, SO_2 had decreased to more than an order of magnitude below its peak.

It seems, however, that rapid transport along the return-flow pathway from Eurasia to the Arctic is insufficient to explain the high winter SO_2 there; long atmospheric lifetimes also seem to be required. Transport times from Eurasia to Bear Island of 5-10 days, initial SO_2 concentrations of 30 $\mu g\ m^{-1}$ (mean winter values for the industrialized countries of Europe[4], probably an overestimate for Europe as a whole), dilution of the polluted air mass by a factor of four during transport (derived from simulations of aerosol transport to Bear Island, probably an underestimate), and a final SO_2 concentration of 3 $\mu g\ m^{-1}$ at Bear Island require that mean residence times during transport be 5-10 days. If the residence time increases during transport, as is likely, an initial value of 2-5 days at the source is still needed to explain the measured SO_2 concentrations. In contrast, currently accepted atmospheric residence times for SO_2 in Europe are 1-2 days[9-11]. Thus, winter residence times for SO_2 in Eurasia would seem to be up to five times longer than annual mean values, and in the Arctic of the order of weeks.

There are good physical and chemical reasons for these long residence times. In Eurasia, the residence time for SO_2 is determined primarily by the rate of dry deposition to the surface, secondarily by precipitation scavenging, and to a still lesser extent by the rate of oxidation to sulphate. In Arctic (or cold continental) winter conditions, all these rates should be very slow, because: (1) The rate of dry deposition decreases with increasing stability of near-surface air and surface smoothness; low values have been measured over snow[12]. (2) Wet deposition of SO_2 should be small during winter in the Arctic because of the slight precipitation there, typically only 5 mm per month. (3) Heterogeneous oxidation of SO_2 in Arctic cloud droplets ought

Fig. 3 Five-day surface geostrophic back-trajectories for cold-air episodes (solid line) and periods of low concentration (broken line) during winter 1977-78. Dates of arrival at Bear Island are indicated.
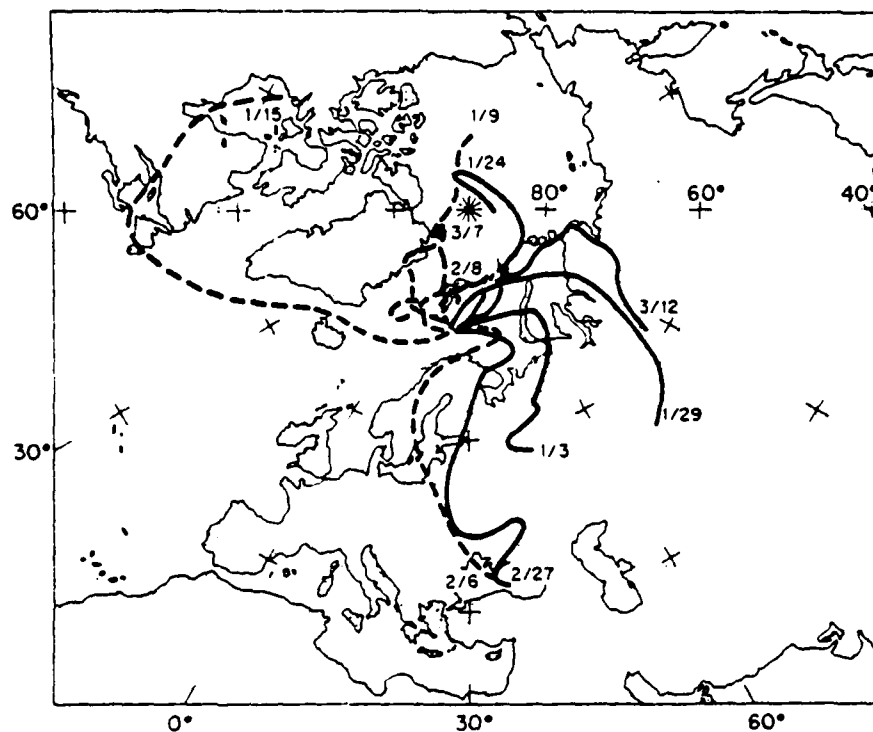
to be very slow because of the low temperatures, the low frequency of clouds, their restricted vertical extent, their small liquid-water content, and the meagre amounts of trace elements such as Mn and V available as catalysts (30–40 times less than in midlatitude air masses). This oxidation rate may decrease as an air mass ages, because acidity produced in the droplets limits the subsequent solubility of SO_2. This decrease ought to be greatest over oceans and cold continents, where little NH_3 is available to neutralize the increasing acidity (C. Brosset, personal communication).[4] Lastly, homogeneous oxidation of SO_2 by the OH radical ought to be extremely slow during the Arctic night because of the lack of direct solar radiation.

Similarly long lifetimes for aerosol in and around the Arctic have been deduced recently[4]. When combined with the long lifetimes for SO_2, they begin to explain how gaseous and particulate sulphur can be efficiently transported northward from midlatitudes during winter and dispersed over the entire Arctic.

This case illustrates just how sensitive the atmospheric rates of transformation and removal of the various forms of sulphur may be to climatic properties. In 1977 the Dubrovnik workshop on atmospheric sulphur[3] recommended that attention be given to these seasonal and regional variations for the sulphur system. Now that long-range transport of gases and aerosols through highly different climatic zones is known to be a regular feature of the atmosphere, such attention becomes mandatory, and should be extended to other species.

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Sources and Transport of Arctic Pollution Aerosol: A Chronicle of Six Years of ONR Research

by

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Arctic Air Is Not Clean

The polar regions are universally considered to be desolate, remote regions whose air and water are still clean and pure. From the earliest explorers to modern travellers, all visitors to the polar regions attest to this view. After all, are not the poles literally the ends of the earth, far removed from the last traces of civilization's products?

In many respects the polar regions are indeed still pristine. The air over Antarctica, for example, shows some of the lowest concentrations of pollutants yet measured on this planet. Snow and ice from Antarctica fail to show any evidence of global pollution in their content of trace substances.

But cracks are beginning to enter this picture. More than a decade ago, snow and ice of Greenland were alleged to show increasing concentrations of certain trace contaminants dating back a century. Further analysis has confirmed this. As a result, it is now generally acknowledged that global air pollution affects both gases and particles throughout the Northern Hemisphere.

During the past six years, the authors, under long-term sponsorship of the Office of Naval Research, have been able to discover and carefully document a major crack in the above picture—the phenomenon known as Arctic haze. Arctic haze is the end product of massive transport of air pollution from various midlatitude sources to the northern polar regions, on a scale and with an intensity that could have never been imagined, even by the most pessimistic observer. The road from initial observation to first hypothesis to final explanation to critical acceptance by the scientific community as a whole has been long, sometimes arduous, and often marked by controversy as new and unexpected ideas were put forth. In this article, we recount how some forgotten observations of 30 years ago eventually led to a whole new field of research—Arctic air chemistry.

First Scientific Observations of Arctic Haze

Perhaps no one will ever know the identity of the first person who knowingly sighted Arctic haze. It probably wasn't an Eskimo, even though they are surrounded by it all winter and spring, because the haze is only barely discernible to a ground observer, even one trained in atmospheric optics. But from the air, it can't be missed. The first description of Arctic haze was in an article on visibility in the polar regions by Dr. J. Murray Mitchell, Jr., then a young climatologist, in 1957[1]. He summarized observations from the "Ptarmigan" weather reconnaissance flights, which from the late 1940's flew from Alaska northward over the Arctic Ocean in an effort to remove the meteorological blind spot in the Arctic which had existed until then. From talks with various observers and from scrutiny of their records, Mitchell was able to systematize the existing knowledge, however scanty, of Arctic haze.

Mitchell found that the haze, which he defined as diffuse bands of tropospheric aerosol (an aerosol is a collection of solid and/or liquid particles suspended in the atmosphere) occurring northward of about 70° and at altitudes of up to 9,000 meters (30,000 feet), was sighted a surprising fraction of the time. Vertical visibility was unaffected by Arctic haze; horizontal and slant visibility could be reduced to as little as 3-8 km (2-5 miles) in a layer, however. This is hardly to be expected for a pristine area. Although light haze can be sighted occasionally in the Antarctic, there is no real counterpart to Arctic haze there.

Mitchell summarized the then-known characteristics of Arctic haze as follows:

"The haze is found during a very high percentage of the time that the weather of the Arctic Ocean is otherwise clear and, being encountered at all normal flight altitudes (700-500-300-mb levels), appears to have considerable vertical depth. Owing to the widely varying conditions of illumination, nothing can confidently be said about the seasonal variation in its frequency. The horizontal extent of the haze is usually limited to segments of the air route which are 500-800 miles (800-1300 km) long, but sometimes stretches over the entire 2000 miles of the reconnaissance track. A curious fact about the haze is that it is seldom found over land, as in the vicinity of Greenland. A ground observer can rarely detect the presence of Arctic haze, just as thin cirrostratus layers encountered by jet aircraft in middle latitudes are often indistinguishable from clear sky to an earth-bound observer. But the similarity between Arctic haze and thin cirrostratus seems to end there: (1) Whereas the cirrostratus appears milky-white from the air, Arctic haze possesses a grey-blue hue in antisolar directions and a reddish-brown hue in the direction of the sun. (2) Whereas the cirrostratus is confined to a definite layer in the atmosphere, Arctic haze possesses very diffuse and indistinct upper and lower boundaries and occupies, in the vertical, a considerable fraction of the Arctic troposphere. And finally, (3) Whereas the cirrostratus is obviously crystalline when viewed at

close range from an aircraft ('You can reach out and touch it'), and produces sun pillars, parhelia, halos and similar optical phenomena in sunlight which are characteristic of ice crystals, the Arctic haze seems completely amorphous to the eye and is almost always without optical effects, at least those which are sufficiently bright to be seen through aircraft windows. The color effects in the haze suggest that, like the low-tropospheric haze of middle latitudes, the constituent particles are no larger than about 2μ. This size is so small that, should the haze be made up of ice, the crystals would be very rudimentary. Since ambient temperatures in the haze are normally in the range of -30 to $-35\,°C$, it is yet possible that supercooled water could be present although, to the writer's knowledge, no aircraft icing has ever been reported in Arctic haze.'"[1]

Alaskan Air Was Too Turbid

After Mitchell's article, Arctic haze was forgotten for 15 years, until one of us, Glenn E. Shaw (G.E.S.), rediscovered it. During the 1972 AIDJEX (Arctic Ice Dynamics Joint Experiment) pilot study near Barrow, Alaska, supposedly routine measurements of atmospheric turbidity with a sun photometer revealed unexpectedly high values, i.e., the local atmosphere contained larger-than-expected amounts of aerosol. These measurements were confirmed during the AIDJEX Lead Experiment of 1974. Numerous flights over the pack ice north and northwest of Barrow showed that much of the anomalous turbidity originated with distinct haze layers at altitudes of a few kilometers. When viewed edge-on, these layers appeared brownish-yellow in color, similar to the more familiar urban haze layers. Occasionally, horizontal visibility through the layers was reduced to only a few kilometers. The similarities between these haze layers and those of Mitchell were so striking that they must have been one and the same phenomenon—Arctic haze[2].

This established that Arctic haze was real and persistent. But the foremost question, its origin, was quite another matter, and was not to be answered easily. Both the visual observations and the optical measurements had shown that the haze was composed of true aerosol, that is, was predominantly very tiny suspended particles. Except for the size, sun-photometer measurements could offer no further information on the aerosol. The issue of greatest concern was whether Arctic haze was natural in origin, i.e., represented some previously unrecognized feature or process of the Arctic atmosphere, or whether it could possibly be pollution-derived. A pollution origin would have great implications for global air pollution, because sources of Arctic haze would have to be at greater distances than were then recognized for transport of pollution aerosol.

Dr. Shaw realized that chemical measurements were needed to determine the origin of the haze. But neither he (an atmospheric physicist) nor his institution (the Geophysical Institute of the University of Alaska) was prepared to carry out the specialized measurements that were required. A compatriot was needed. In May 1975, GES met Kenneth A. Rahn (K.A.R.) at a workshop in Polar Meteorology in Reno, Nevada. KAR's background in trace-element analysis of remote aerosols and interest in the north seemed to make him an ideal candidate for a partner. The subject was broached, a joint proposal for a pilot study was submitted and accepted by ONR in 1976, and the association has continued through the present.

Asian Desert Dust Over Alaska

Our approach to Arctic haze was to combine optical, chemical, physical and meteorological techniques to get the broadest possible information. The chemical composition of the haze was to be used to deduce whether it was natural or pollution-derived. If pollution-derived, an idea of its age was to be obtained from its optical and physical properties, primarily from its particle-size distribution. An idea of its source area was to come from backwards air-mass trajectories. Things didn't work out at all this way in practice, however.

Our first experiment consisted of equipping a light airplane for aerosol sampling, then collecting samples directly from haze bands over Barrow. This experiment was under the direction of Mr. Randolph D. Borys, now a graduate student at Colorado State University, and took place in April-May 1976. It was based at the Naval Arctic Research Laboratory in Barrow, and used one of their single-engine Cessna 180's. Overall, it was a huge success. Ironically, however, a chance encounter with an atypical aerosol threw us off the track for several months.

During the early sampling, no distinct haze bands were seen, and the flights proceeded routinely. Towards the end of the experiment, however, pronounced haze bands appeared, associated with winds from the south. It seemed that a period of intense Arctic haze had been caught by luck. Just before the end of the experiment, the bands disappeared. Back at the University of Rhode Island, analysis of the

aerosol samples caught us completely by surprise: particles of the early period showed distinct traces of pollution products, whereas those of the later (banded) period showed large amounts of soil-derived dust. In other words, the haze bands had been soil dust!

The chemical basis for this conclusion is illustrated in Figure 1 which shows concentrations of the elements aluminum (Al) and vanadium (V) for the nine samples that were taken. These two elements are extremely useful in studies of aerosol from remote regions, because of their sources. Atmospheric Al comes primarily from soil dust. V, on the other hand, has two main sources: soil dust and combustion of oils, particularly the less-refined residual oil (which is too heavy and viscous to be burned in the Arctic). The V/Al ratio of soil-derived aerosol is very well-known and reproducible from place to place, and similar to that of the bulk crust. Aerosol with a soil-like V/Al ratio can be considered as strongly natural in origin. In and around polluted areas, however, particularly those where large amounts of oil are burned, the V/Al ratio is much higher and can reach extremes of more than 100 times the crustal ratio. In these circumstances, V is said to be enriched relative to the crust. The degree of enrichment is usually expressed by calculating the aerosol-crust enrichment factor of V, defined as

$$EF_V = (V/Al)_{aerosol}/(V/Al)_{crust}.$$
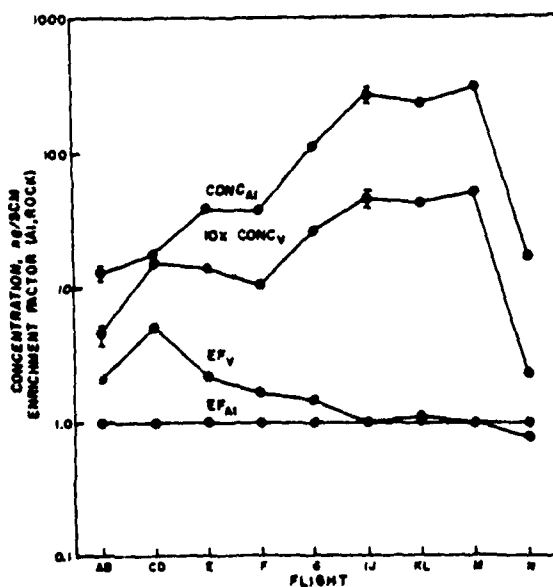
Figure 1. Concentrations and enrichment factors of V and Al in aerosol over Barrow, Alaska, April-May 1976.[1]

where Al and rock serve as the reference element and reference material, respectively, for the crust. We normally use Mason's mean composition of global rock as our reference material[1]; other workers sometimes use other mean rocks or mean soils.

The enrichment factor of vanadium (EF$_V$) provides an extremely sensitive test of the pollution vs. natural character of an aerosol. When its values are below 1.5 or so, the aerosol may be considered natural. When the value exceeds 1.5, the aerosol is showing definite influences of pollution. Our first Barrow experiment had two distinct phases: Flights A through G where pollution aerosol was seen, and Flights I through N where the aerosol was soil-derived. The soil-derived nature of the latter aerosol was seen clearly when the filters were examined with an electron microscope: angular mineral particles were abundant in samples I through M and nearly absent earlier.

As noted above, the soil dust came to Barrow with south winds. But the North Slope was still frozen and completely snow-covered, and could not have been the source of this material. The rest of Alaska was probably not the source either, for it too was mostly snow-covered. Furthermore, the very small size of the soil particles indicated that they had travelled long distances in the atmosphere, farther than from some other part of Alaska.

The source was finally revealed by backwards air-mass trajectories, as shown in Figure 2. Those samples with the most soil dust had passed over the great deserts of eastern China and Mongolia (Gobi, Takla Makan, Ordos, Loess Plateau) a few days earlier. (By contrast the earlier, slightly polluted, samples had come from the north.) Each spring, these deserts give rise to huge dust storms whose soil particles can travel far over the Pacific. In the deep-sea sediments of the Pacific, east-west bands of quartz and certain clay minerals can be found extending from Asia nearly to North America[4,5]. Short events of desert dust reaching North America, called "ice-nucleus storms," have been detected in Washington State and even in Fairbanks[4]. So it perhaps should have come as no surprise to find Asian desert dust over Barrow, but we were nevertheless taken aback. To confirm the Asian origin of our desert dust, we checked the weather records during our experiment, and found that there had indeed been a major dust storm in eastern Asia from 22-24 April 1976, which could be followed from its generation in the Gobi Desert through its transport southward, then northeastward past Japan and Korea out over the Pacific, where it was lost until part of the cloud was observed a few days later over Barrow (see Figure 3)[7].
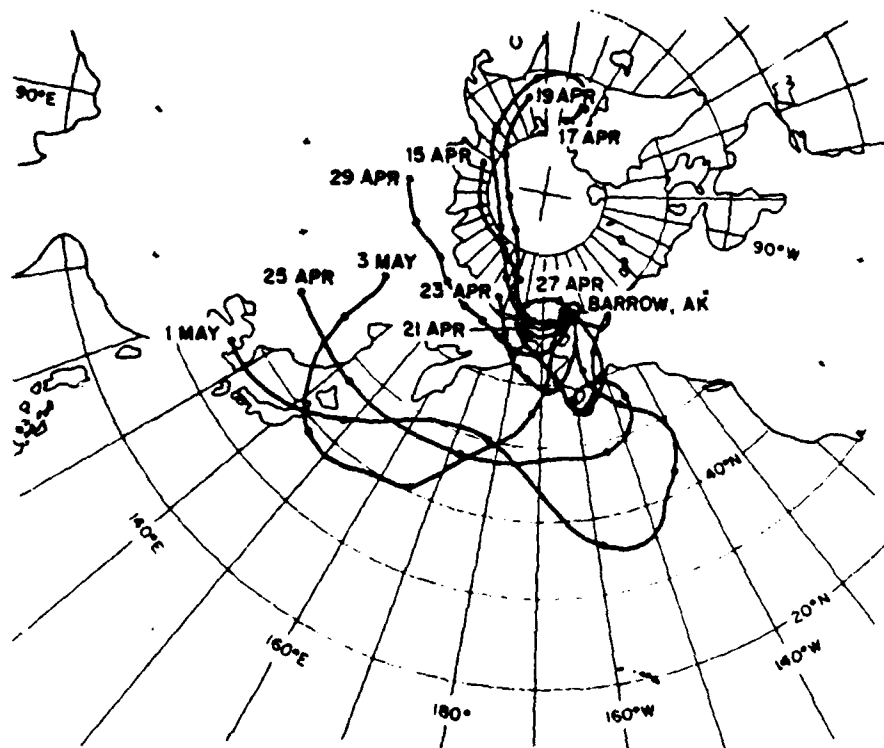
Figure 2. 700-mb isobaric trajectories of air to Barrow, spring 1976'. Numbers refer to date of arrival at Barrow; solid circles each 24 hours.

In short, our first experiment had found a little pollution and a lot of soil dust over Barrow. Furthermore, the banded nature of the dust clouds matched the two earlier reports on Arctic haze. For these reasons, we concluded that Asian desert dust might be responsible for much or most of Arctic haze. Consequently, Arctic haze was a natural phenomenon.

Arctic Haze is Pollution Aerosol, Not Desert Dust

Within a year or so, however, this idea had to be abandoned. The first inkling that something was wrong came from sun-photometer data of this experiment, which showed that there had been just as much turbidity before the soil-dust bands arrived as when they were over Barrow in full force. In the first flushes of discovering the longest known transport of Asian dust, we had failed to face this observation squarely; only several months later did its true meaning become fully evident. The very low concentra-

tions of pollution-derived vanadium, nearly as low as had been measured anywhere else in the Northern Hemisphere, also failed to alert us to the potential link between pollution aerosol and Arctic haze. We now know one very important reason for this, namely that our experiment was unwittingly performed at the very end of the pollution season at Barrow, just before pollution aerosol disappears for the summer. Had we done our experiment several months earlier, we would have been hit with such high concentrations of vanadium that their significance could not have been missed.

The real blow to the desert-dust hypothesis and a natural explanation for Arctic haze came with the initiation of ground-based aerosol sampling at Barrow the following fall. Ironically, we started this ground project as a cheap alternative to year-round aircraft experiments, whose cost and logistics were both prohibitive. But we were still looking for desert aerosol, and were quite unprepared for what was about to happen.

The ground-based experiment almost never
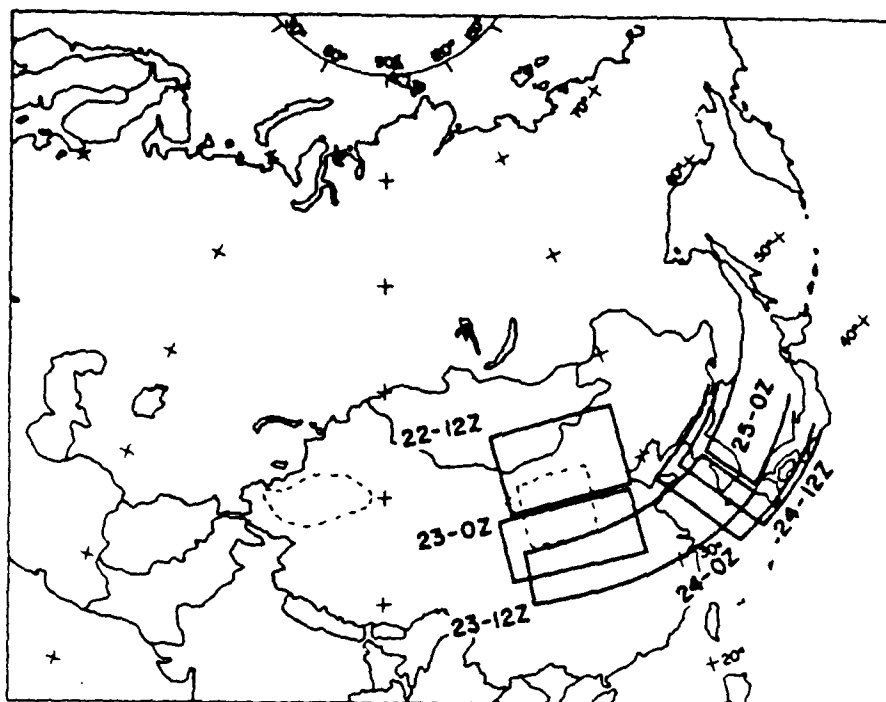
Figure 3. Progression of the dust cloud for the storm of 22 April 1976.

started. We knew that ground-level sampling wasn't a very good way to look for bands of aerosol which are usually found aloft, and so did our program manager Dr. G. Leonard Johnson, Group Leader of ONR's Arctic Program. But we argued that ground sampling was better than nothing, was inexpensive, and had a reasonable chance of picking up some traces of dust layers aloft. In any event, it would tide us through the winter until we could perform another aircraft experiment the following spring. Dr. Johnson relented, the experiment went forward, the next spring's aircraft experiment never happened (for a variety of other reasons), and Arctic air chemistry hasn't been the same since.

In September 1976, KAR visited Barrow and set up a high-volume aerosol-sampling system at the GMCC Baseline Observatory. The GMCC (Geophysical Monitoring for Climatic Change) program is a branch of the National Oceanic and Atmospheric Administration (NOAA) which is dedicated to monitoring long-term changes in the chemistry and physics of the atmosphere that may affect world climate. The GMCC program also operates observatories at Mauna Loa (Hawaii), American Samoa, and the South Pole. At Barrow, their two full-time observers changed filters for us and mailed them to Rhode Island, thereby greatly reducing the costs of our experiment, and making long-term sampling at Barrow feasible.

The first few samples from Barrow were very light in color, and contained little besides sea salt. About the first of November, however, the entire character of the Barrow aerosol changed suddenly. The samples were dark gray in color, and contained much higher concentrations of Al, V and Mn, in proportions more like urban samples than clean-area samples. For example, the enrichment factor of vanadium jumped from 1 to 10, indicating that 90 percent of the aerosol was pollution-derived. When all these facts were considered (together with data for a much larger number of elements that we later determined), it was obvious that we were dealing with a pollution-derived aerosol.

Throughout that first winter, concentrations of Al, V, Mn and carbon remained at roughly an order of magnitude above their September-October values. During spring, the traditional period of most intense haze at Barrow, the elemental concentrations increased by another factor of 2-3. Near the end of April, all concentrations decreased abruptly, and the aerosol remained nearly pure sea salt for the rest of the summer. The monthly mean concentrations of vanadium during the first year of sampling are shown in Figure 4. No desert dust was seen that winter or

spring!

The Winter Pollution Did Not Come from Barrow

Where had the pollution aerosol of winter come from? We realized immediately that it could not have had Barrow as a source, for several reasons. First, no vanadium is emitted by Barrow. As mentioned above, vanadium comes from heavy oils, and the fuels at Barrow are primarily natural gas (which is free of trace elements like V and Mn) and highly refined jet fuels, which are also extremely low in impurities. Second, our samples were sector-controlled, that is, air was sampled only from directions other than Barrow. The GMCC observatory is east of everything else around Barrow, so that air coming from the east off the Arctic Ocean (the predominant wind direction during winter) is free of local influences. Third, as a test, we had taken four of the initial samples deliberately out-of-sector, i.e., from the direction of Barrow. No significant differences from the in-sector samples were seen. This indicated that Barrow was a weak source of pollution, which was reasonable considering that Barrow had only 3,000 inhabitants, mostly Eskimos, who follow a simple

Figure 4. Monthly mean concentra· . s of excess (nonmarine) sulfate and excess (noncrustal) vanadium at Barrow, Alaska, 1976-77.[10]

lifestyle. (While these ideas were proof enough for us, it would be several more years before we would be able to convince the last skeptics that our samples were something other than Barrow contamination.)

Abnormal Amounts of Sulfate Required to Explain the Intensity of the Haze

On balance, the outstanding feature of that first year's record from Barrow was the 10- to 30-fold higher concentrations of pollution aerosol during winter than during summer. (We now have taken five years of aerosol samples from Barrow. The first four years have been analyzed, and confirm the seasonality and absolute concentrations of the first year). We thus began to consider very seriously whether pollution aerosol could be responsible for Arctic haze. Although the timing seemed right, a problem remained: the concentrations of vanadium, manganese, etc., seemed much too small to account for the haze. Whereas the intensity of the haze (as measured by optical depth, or turbidity) was only 3-5 times less than in regionally polluted areas such as the northeastern United States, manganese and vanadium were 20-40 times lower. In other words, there was an order of magnitude "too much" haze for the pollution aerosol.

At this point, various possible explanations were proposed but none seemed very reasonable. Perhaps some major constituent of the haze was enriched by an order of magnitude compared to urban aerosols. This explanation (which later turned out to be the correct one) was dismissed at the time because of the great similarities among many different aerosols shown by previous studies. A strong effect of relative humidity (which causes hygroscopic particles to take up water and swell, and hence scatter light more efficiently) in the Arctic was suggested but also considered unlikely. A layer of concentrated aerosol aloft was also considered improbable and ad hoc.

Without a great deal of hope, we undertook to measure the amount of sulfate in the haze. Sulfate is a major constituent of most aerosols, and is often the single most abundant species. To our great surprise, sulfate turned out to be an order of magnitude higher at Barrow than we had expected, and easily concentrated enough to explain the turbidities. Its monthly means for 1976-77 are shown in Figure 4. The absolute concentrations of sulfate are strikingly high at Barrow: mean winter values for 1976-77 were 1-2 μg m^{-3}, and the mean for March 1977 (and subsequent Marches as well) was about 2.5 μg m^{-3}. (We had anticipated concentrations of 0.1-0.3 μg m^{-3}.) To put
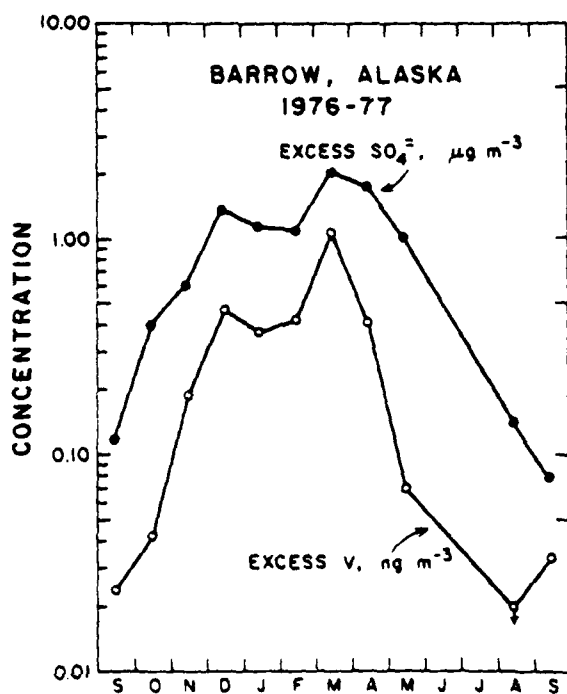
these values in perspective, consider that sulfate concentrations in the northeastern United States during winter are roughly 6 μg m^{-3}, only twice as high as those at Barrow during March. Our first Barrow samples were roughly a week in duration; we have since found that individual days can have sulfate concentrations as high as 5 μg m^{-3}. This means that on some days, sulfate is higher in Barrow than it is in the northeastern United States!

Other things being equal, it is harder to understand the sources of sulfate than of vanadium, because there are significant natural sources of sulfur to the atmosphere, at least when averaged over the globe. The high sulfate concentrations, coupled with their parallelism to pollution-derived vanadium, suggested to us from the beginning that the sulfate was also pollution-derived, and nothing since then has changed our minds. It truly seemed that Arctic haze stemmed largely from a pollution-derived, sulfate-rich aerosol of distant origin.

Source of the Pollution Haze
Is Outside the Arctic

We then began to focus on the area of origin of the haze. Certain colleagues had suggested that we were detecting nothing more than North Slope contamination, from the oil-related activities in Prudhoe Bay. We did not accept this explanation because, by this time, aerosol very similar to that of Barrow had been detected by other scientists in the Northwest Territories of Canada (at Mould Bay) and around the northern edge of Greenland, and at Spitsbergen and Bear Island in the Norwegian Arctic. To eliminate the North Slope as a major source, Mr. Thomas J. Conway of our project carried out an experiment on Narwahl Island in April 1979. Narwahl Island lies about 25 miles NW of Prudhoe Bay, so that air coming to it from the north-to-east quadrant is unaffected by the Alaskan mainland. A series of samples taken at Narwahl Island concurrently with samples at Barrow showed very similar concentrations of manganese, vanadium and sulfate, and were indistinguishable to the eye from the Barrow samples (had equal concentrations of carbon). This showed once and for all that pollution aerosol observed at Barrow represents that found over much of the polar cap during winter, not just the North Slope. The sources of this aerosol must lie outside the Arctic. To localize these sources, we turned (unsuccessfully) to trajectory analysis.

Air-mass Trajectories *Not* Useful

The most common meteorological technique for tracing the history of an air mass is to calculate back-trajectories for it. Using the speed and direction of wind at the time of sampling, the position of the air is calculated for some previous time, say 12 hours earlier. Observations at that time and place are then used to calculate where the air had been another 12 hours earlier, and so on. At Barrow, one may precede this process with the observation that the most polluted air comes from the north, i.e., from over the polar cap. Air masses from the south are up to an order of magnitude cleaner. (This situation is just the opposite of what is normally found in midlatitudes, where north is the clean direction.) Severe problems arise almost immediately when one attempts to calculate back-trajectories for the northern (polluted) air masses at Barrow, however. First of all, it typically takes four days for air masses to cross the ice cap. As a rough rule of thumb, trajectories become quite uncertain after two days and of little meaning after five days, except when flow patterns are extremely well-defined. Thus, it is difficult to determine where an air mass first encountered the ice cap, to say nothing of where it had been earlier. This problem of distance is compounded by the sparsity of meteorological data in the Arctic—very often there are no data at all from the entire ice cap. As a result, trajectories calculated for the Arctic are less reliable than those for other locations. When this is coupled with the long distances from the Arctic to major pollution sources (5,000-10,000 km), it should perhaps not be surprising that trajectory calculations have been unable to localize the source areas of aerosol of the North American Arctic, even though we and others have tried both forward and backward trajectories[1-10]. As an alternative, we tried using air-mass analysis, where characteristic properties such as temperature, relative humidity, or stability were used as tracers, but this didn't work either, because of the tendency for air masses to become aged and similar in properties by the time they reached the Arctic. Still other meteorological approaches, some quite inventive, have been tried to explain the origin of the aerosol of the North American Arctic[11,12]. Results have been mixed at best.

Thus we reluctantly concluded that presently available meteorological techniques cannot satisfactorily resolve the source areas of Arctic aerosol. It remains an important question, however. For some years, we sought the answer by assembling all relevant evidence, however indirect and circumstantial. Fortunately, there are quite a few pieces of relevant

evidence; in the paragraphs below, we review a few of the most important. A fuller discussion has recently been given elsewhere[13].

Likely Sources and Pathways of Pollution

At the beginning of this project, we felt intuitively (and probably naïvely) that eastern North America was the most likely source of Arctic haze. Shortly thereafter, as we began to measure distances on a globe and evaluate potential transport pathways, we were forced to broaden our outlook to three large polluted areas: eastern North America, Europe (including the western USSR) and eastern Asia (China, Japan, Korea, etc.). By knowing the prevailing winds near each source area, one can rather easily propose the most likely pathway(s) from each to the Arctic. Figure 5 shows these sources and pathways as

Figure 5. Possible sources and pathways for transport of pollution aerosol between midlatitudes and the Arctic.[13]
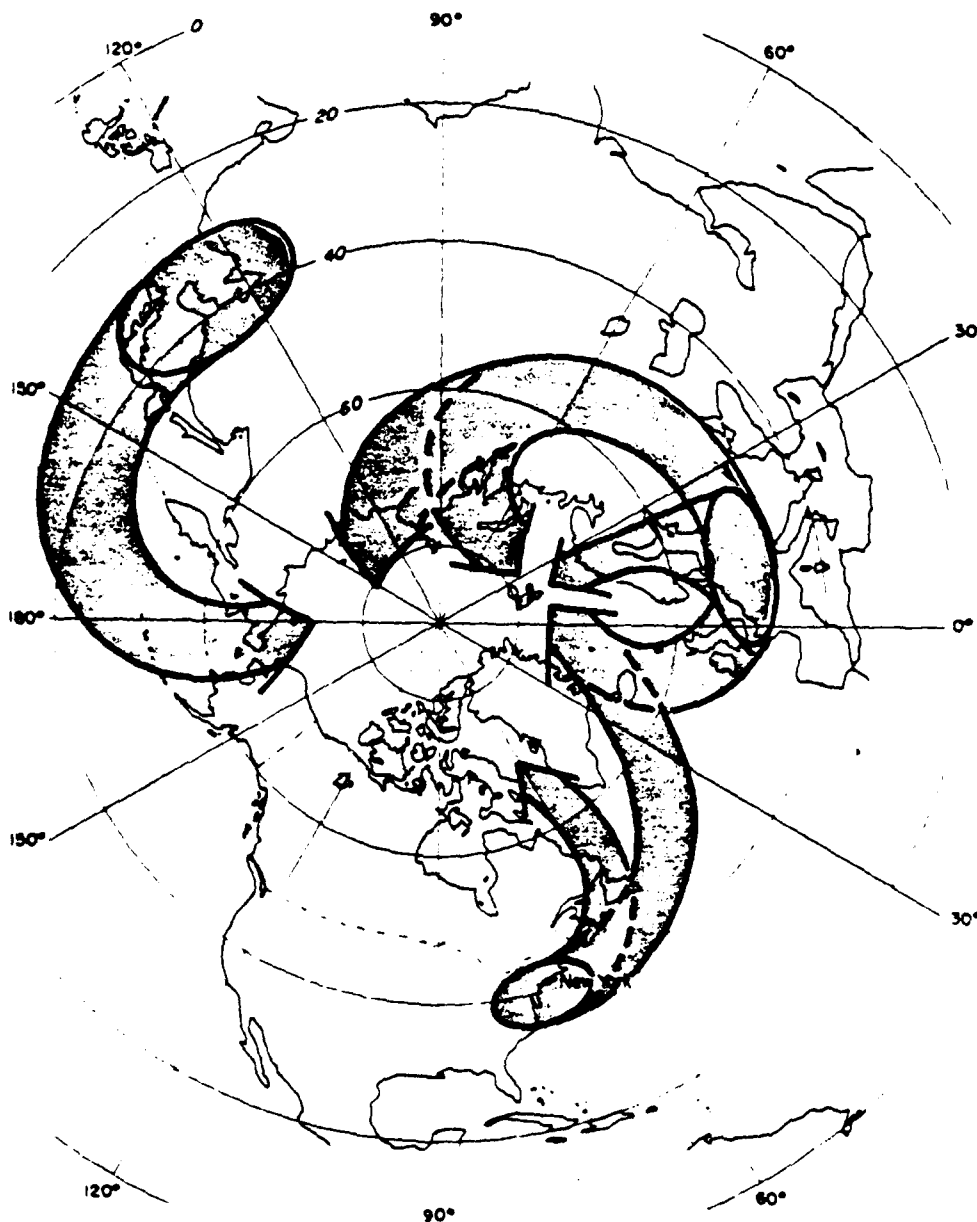
they were conceived in 1979. From eastern North America, the most likely pathway would be via the North Atlantic Ocean, Iceland and the Norwegian Sea, following the dominant storm track for that region. Another possible pathway would be via the west side of Greenland, but this should be less important, because the normal flow of air there is southward, not northward (northeastern Canada is the great exit area for air leaving the Arctic). From the beginning, we felt that the most important pathway(s) had to be active a large fraction of the time during winter, because polar air at Barrow inevitably had high concentrations· of aerosol. A pathway with the wrong basic directionality, such as the one along the west side of Greenland, could probably not play a major role in Arctic air chemistry. The pathway from eastern Asia over the Pacific was similar to that from eastern North America, being also based on a storm track. Air flow near the ends of the Atlantic and Pacific pathways would be controlled by the Icelandic and Aleutian low-pressure areas, respectively.

On observational grounds alone, it was easy to eliminate eastern Asia as a major source of Arctic aerosol: air from the Pacific pathway, approaching Barrow from the south, is the cleanest observed there. The reason for these low concentrations is probably the storminess of this path because abundant precipitation cleanses the air efficiently. Analogous reasoning would imply that the North American source via the Atlantic pathway ought not to be important for the Arctic. For a long time we lacked direct observations along this pathway to confirm or reject this idea, but we now have them from both southern Greenland and Iceland. Near southern Greenland, concentrations of aerosol are very low in winter, as expected from an inefficient pathway. At Iceland, from which we now have abundant year-round data, air masses approaching from the west are very clean. High concentrations of aerosol are occasionally observed at Iceland, to be sure, but only in air masses coming from Europe. A study off the coast of western Ireland confirmed the cleanliness of Atlantic air masses. We have never observed high concentrations of aerosol in air masses that have crossed the Atlantic.

Europe the Likely Source

This reasoning left Europe as the only source area for Arctic pollution aerosol. By late 1978, the basis for this conclusion was strong enough that we began to speak about it publicly. Again, there were many skeptics, including those who chose to read scientific nationalism into the contention of Americans that Europe, not North America, was the source of Arctic haze. But this conclusion has stood the test of time (with modifications discussed below), and is now supported by abundant evidence. The first strong piece of evidence we had, and one which is still solid, is the geographical distribution of sulfate aerosol during winter. Figure 6 is a map of winter-mean concentrations of nonmarine sulfate in and around the Arctic, with data available as of 1979. It shows that concentrations are low over the North Atlantic (data from southern Greenland and several cruises in the mid-Atlantic) and, indirectly, that concentrations are low over the Pacific (2½-fold lower concentrations in interior Alaska, which receives Pacific air, than at Barrow). Furthermore, the map shows that Europe is indeed connected to the Arctic by a broad tongue of high sulfate concentrations stretching northward through Scandinavia into the Norwegian Arctic. From southern Scandinavia through Spitsbergen, a north-south distance of 2,000 km, sulfate remains constant at about 2 μg m^{-3}. Another observation from Figure 6 that is consistent with a European source is the slight decrease in sulfate from the Norwegian to the North American side of the Arctic, from 2 to 1.5 μg m^{-3}, which suggests that the sources for both regions are on the Norwegian side of the Arctic.

Convincing as these arguments are, however, they are still indirect and circumstantial, and hence not completely satisfying, even as a package. Direct evidence is needed.

Tracer Evidence of Sources—Mn/V

For a long time, we have believed that the only truly direct evidence on sources of Arctic aerosol was going to come from the composition of the aerosol itself acting as a tracer. According to this idea, there must be regional differences in pollution aerosol stemming from regional differences in fuels, basic economies, etc. But no one had ever found such differences. On the contrary, the major impression from trace-element studies in Europe and North America was the similarity, not the difference between aerosols. If an element was nonenriched in one city, it was nonenriched in all other cities. If an element was enriched in one city, it was enriched in all other cities, and to surprisingly similar degrees. To a limited extent, we had looked for regional differences, but to no avail. By the late 1970's, we had nearly given up on ever finding them, and had even
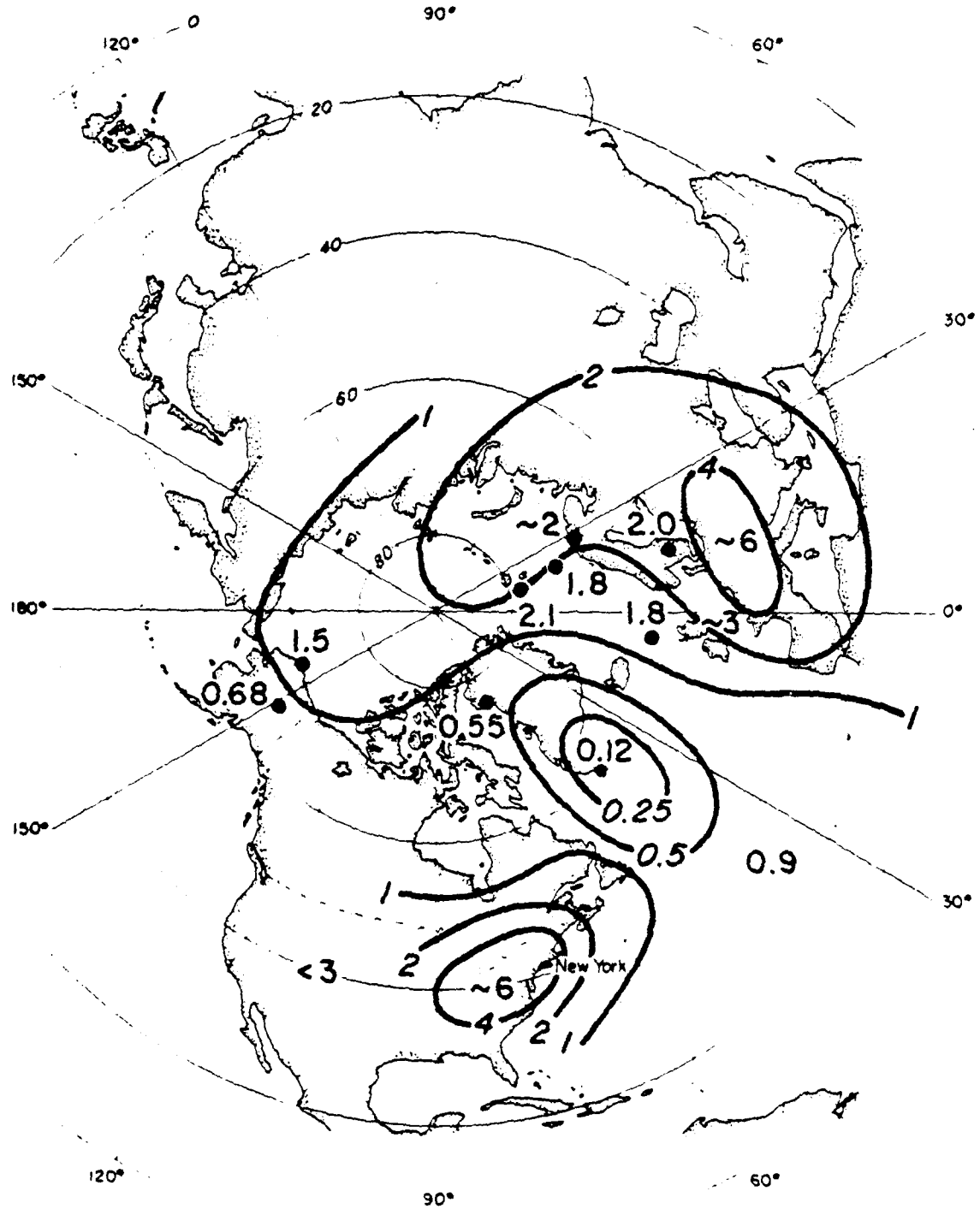
Figure 6. Mean winter concentrations of nonmarine sulfate (µg m⁻¹) in surface aerosol of the Arctic and environs.¹¹

looked into the feasibility of using pollution gases instead.

Then in April 1980, in a chance conversation between KAR and Dr. L. Barrie of Atmospheric Environment Service, Canada, the subject of manganese in the European aerosol arose. Both had lived and worked in Europe a few years earlier, and had independently found more Mn in European cities than they were accustomed to in North America. That conversation led KAR to try to construct a tracer from the Mn/V ratio (more precisely, the ratio of noncrustal Mn to noncrustal V). This ratio had the prospect of being considerably larger in value in Europe than in eastern North America, because Mn was high in Europe and V was high in eastern North America. In principle, the ratio of two elements would have distinct advantages as a tracer, because its value should change much more slowly during transport than would the concentration of either element alone, especially if the two elements were on similar particle sizes in the aerosol. A properly chosen elemental ratio could thus approach conservative behavior during transport. Mn and V were good candidates for a ratio because they are both enriched, pollution-derived elements, and hence associated with the submicron fraction of the aerosol. Earlier attempts to use the enrichment factor of pollution elements as tracers had been abandoned because of the great disparity in size between the pollution-derived elements (usually submicron) and the reference element aluminum (supermicron). As a result, enrichment factors changed too much during transport.

The Mn/V ratio worked. On a plot of Mn vs. V, European samples separated cleanly from those taken in the eastern United States (Figure 7). Mean Mn/V ratios were 5 ± 1 times greater in Europe than in the eastern United States. Although the reasons for this are still not known fully, the tracer can be used with confidence. In addition, values from various Arctic sites on the same plot, showed that the Norwegian Arctic and North American Arctic regions were separated by a factor of two in ratio. We had not realized that there were such large regional differences in the Arctic aerosol. Like Europe, the North American Arctic had Mn/V ratios greater than unity, and like eastern North America, the Norwegian Arctic had ratios less than unity.

Did this mean that Europe was the source of aerosol for the North American Arctic and eastern North America for the Norwegian Arctic? Not necessarily, for there is both theoretical and observational evidence that the Mn/V ratio decreases systematically during long-range transport by factors of up to 3-4.
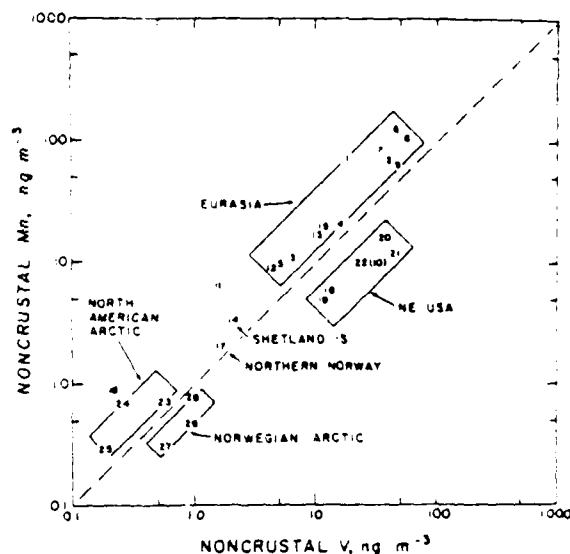
Figure 7. Atmospheric concentrations of noncrustal Mn and V in Eurasia, the northeast U.S.A., and the Arctic.[14]

The reasons for this are not completely understood. In part, they seem to be related to particle size, for Mn is often found on somewhat coarser particles than is V and thus should be removed faster during transport[14]. But the decreases predicted from particle size alone are more like a factor of two at most. The reasons for this discrepancy are not yet known. Applying the operational decrease of 3-4 times during transport brings a great deal of order to Figure 7: aerosol of the Norwegian Arctic becomes compatible with a European precursor, as so much other evidence indicates; aerosol transported from eastern North America takes on a Mn/V ratio much lower than is ever found in the Arctic, which is consistent with the rapid washout of North American aerosol by Atlantic storms noted above. But another puzzle is created: the source area for aerosol of the North American Arctic (Barrow and Mould Bay) must have a higher Mn/V ratio than any site depicted in Figure 7.

The Central Soviet Union a Potent Source

What could this source be? We feel that it is most likely the central Soviet Union. There are at least two reasons to expect a very high Mn/V ratio in aerosol from this region: much steel is produced there (which favors the release of large amounts of Mn), and the economy of the area is based strongly on coal (coal-burning areas have high Mn/V ratios).

Huge quantities of pollution aerosol are released in the central Soviet Union—some of the highest pollution levels in the entire Soviet Union are found here[]. Furthermore, as discussed below, there is a very fficient transport path from this region that went unrecognized for a long time. A great variety of circumstantial evidence now points to the central Soviet Union as the major source of aerosol for the North American Arctic. Ironically, it was not one of our original three candidate-areas.

Pathways

What about pathways to the Arctic? Here we have to consider Europe and the central Soviet Union separately. For Europe, there is a broad body of basic knowledge concerning northward transport which has come from the decade-long systematic study of acidity in Scandinavia. Sponsored first by OECD (Organisation for Economic Cooperation and Development) and now by ECE (Economic Commission for Europe), the transport and deposition of sulfur and acidity have been thoroughly investigated by large-scale cooperative studies within Europe. The deposition of acidity in Scandinavia normally occurs in a series of episodes each winter, all associated with strong northward air flow from the more populated an[] industrialized countries to the south, such as Gr...: Britain, France, Germany, Poland and the western Soviet Union. The most common vehicle is the "black episode," so named for the dark appearance of the aerosol on filters[]. A black episode is created when a high-pressure area centered over or east of Europe combines with a low-pressure area approaching from the Atlantic to create a narrow but intense zone of northward transport in between. When the low and high are positioned so that this transport zone begins in central Europe and passes over Scandinavia, much of Scandinavia is blanketed by black, acidic aerosol in concentrations several times the norm and for periods of up to a few days.

It is now known that black episodes can occasionally continue all the way into the Norwegian Arctic. As such, they become an important source of pollution aerosol for this region. There are at least two variations on the basic northward pathway: one west of Norway (when the Asiatic high is westward of its normal position), and one over the Baltic Sea between Sweden and Finland. According to Dr. B. Ottar of the Norwegian Institute for Air Research, who has directed these European studies for the last several years, there is a tendency for the northward air flow to avoid the mountainous Scandinavian ?eninsula. Because of their relatively straight pathwa,s, we refer to these periods of northward flow to the Norwegian Arctic as "direct" episodes.

For a long time, we thought that direct episodes were the key to understanding air pollution in the Norwegian Arctic. In 1979, how ver, we were surprised to learn that they are only a small part of the story. In a cooperative study of air pollution at Bear Island with the Norwegian Institute of Air Research, we discovered that the most frequent pathway of SO_2 (the gaseous precursor to sulfate aerosol) into Bear Island is from the northeast, not from the south as would be expected for direct episodes. During the winter of 1977-78 for example, 10 of 13 pulses of SO_2 at Bear Island were from the northeastern quadrant[].

These northeastern air masses are much colder than are those of direct episodes from the south. The basic explanation for this second type of episode can be seen easily from meteorological maps: t e cold-air pulses from the northeast are inevitabl associated with low-pressure areas centered over open water south of Bear Island, and are really the tail end of a cyclonic pathway that originated far to the south, moved eastward and northeastward around the leading edge of the advancing low, then recurved southward and westward around the north side of the low. Because of this 180° curvature, we coined the term "return-flow" pathway. Figure 8 shows five examples of actual return-flow pathways for SO_2 coming to Bear Island; Figure 9 is an idealized version of this pain as it was envisaged in 1979, and shows how aerosol might continue from the Norwegian Arctic into the North American Arctic. We have recently confirmed the existence of this pathway to Barrow. It seems to be particularly active during spring, for reasons discussed below.

The main transport pathway from the central Soviet Union to the Arctic can be seen quite readily, together with the meteorological mechanism responsible for it, from meteorological maps. As noted above, we had missed this pathway until recently, because we didn't have the right source area in mind (it was only in 1980 that we realized that the central Soviet Union was the key source for Barrow, after we had come upon the Mn/V tracer. Previously, we had sought repeatedly and unsuccessfully to correlate episodes of flow from Europe with pulses of aerosol at Barrow.)

It should be noted perhaps that we use the term "central Soviet Union" in a vague, operational sense since the exact source areas of aerosol in this region are not yet clear. Originally, we focused on the southern Urals, where heavy industry is abundant. There are other potential sources nearby, however, including adjoining parts of Kazakhstan, western Siberia, and possibly also the European Soviet Union.
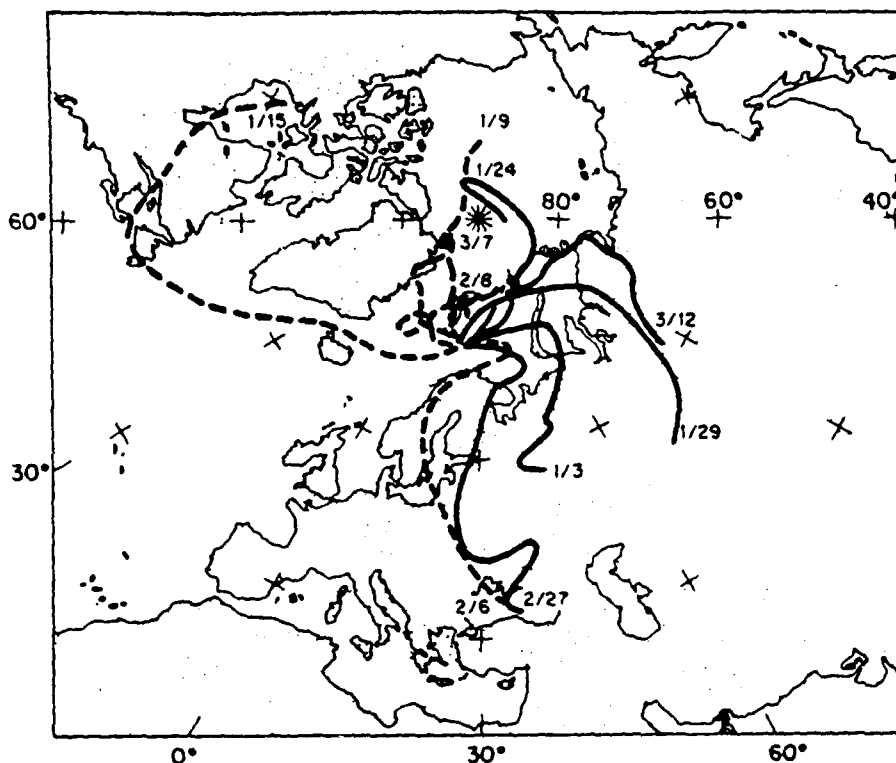
Figure 8. Five-day surface geostrophic back-trajectories of return-flow episodes (solid lines) and periods of low concentrations (broken lines) of SO₃ at Bear Island during winter 1977-78. Dates of arrival at Bear Island are indicated.''

Noril'sk, a copper-nickel smelting complex in Northern Siberia, may also be important.

Meteorological Features of Pollution Transport

The meteorological maps showed that, once again, the leading edge of a low-pressure area is involved with transport to the Arctic, normally but not always in combination with a high-pressure area. The low-pressure areas involved are later stages of the same systems discussed earlier for Bear Island. In this case, however, they are centered near Novaya Zemlya. They are often quite large, and their area of influence can extend as far south as 50°N, easily encompassing the important source areas at roughly 55°N. The high-pressure area involved is the Asiatic high, which is very strong during winter and is normally centered in Mongolia. In addition to dominating the pressure patterns over much of interior Asia, it often has a lobe which extends through the northeastern Soviet Union into the Arctic. The combination of the low over Novaya Zemlya and the high over Mongolia

produces a very strong region or northward air flow centered roughly on the eastern Taymyr Peninsula. Pressure patterns at the surface during January are shown in Figure 10.

Several interesting aspects of this flow pattern should be noted. Perhaps the most significant of these stems from the fact that the lows rarely penetrate beyond Novaya Zemlya. This is because they depend on the warm open sea for their energy. But the open water, which extends over the top of Norway in response to a branch of the warm Gulf stream (which creates the ice-free Arctic port of Murmansk, so important to the Soviet Union), ends before Novaya Zemlya. The migrating lows, which are traceable all the way back to North America, pass rapidly over the North Atlantic and Iceland, then follow the warm water over the top of Norway, past Bear Island and into the Novaya Zemlya area. Upon encountering the pack ice west of Novaya Zemlya and the ridge of high pressure on the other side of the Taymyr, they stagnate and eventually die, to be replaced a few days later by the next low. With certain variations, this pattern repeats itself throughout the winter.

Figure 9. Idealized return-flow pathway from Europe to the Norwegian Arctic, with continuation to the North American Arctic.[1]
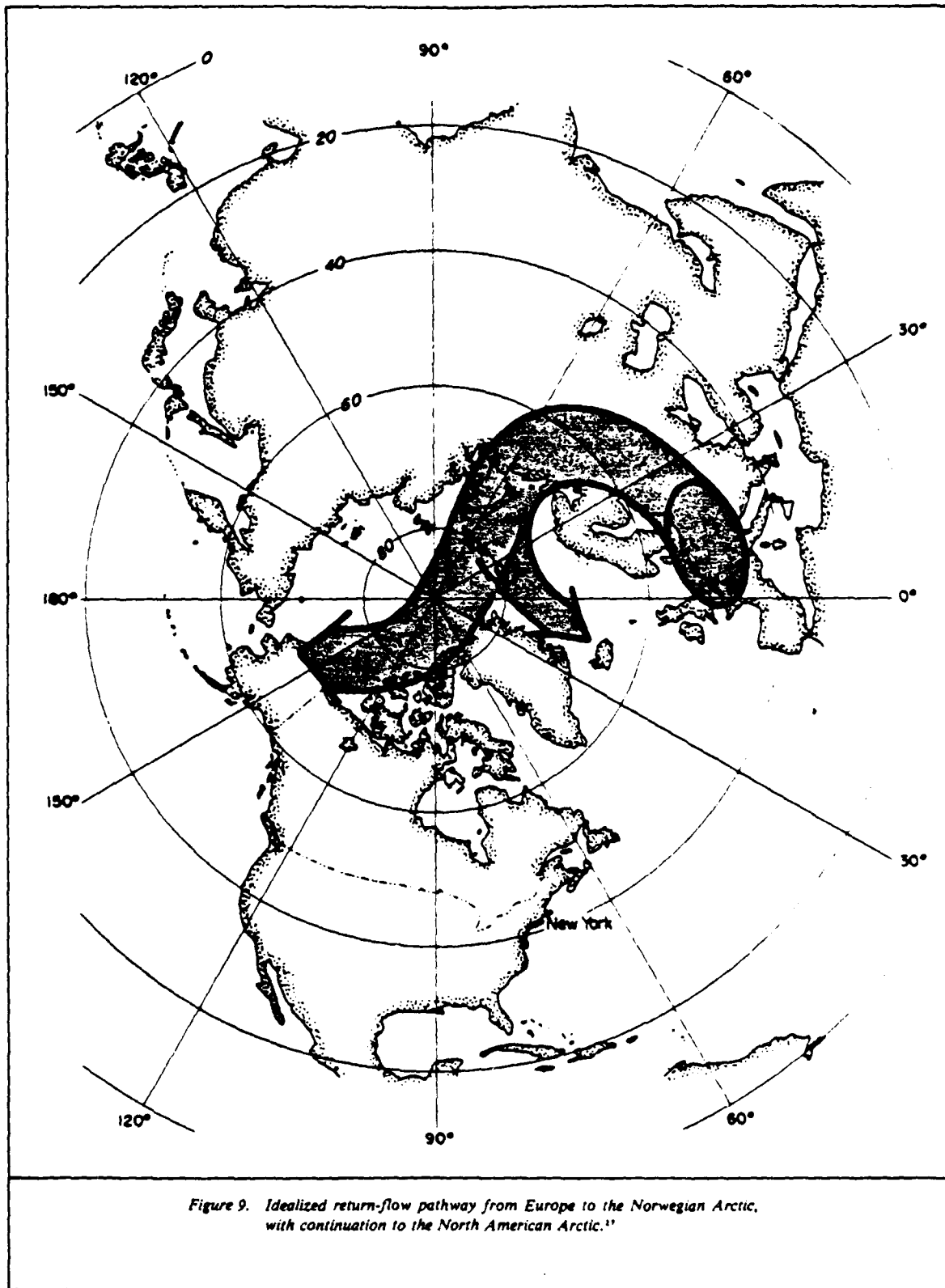
The net result is to create a semi-permanent zone of east-west pressure gradient centered on the eastern Taymyr Peninsula. Because the migrating lows do not pass the peninsula, this pressure gradient varies in intensity (depending on the proxim.ty of the nearest low) but not in direction. This creates a zone of flow to the Arctic which we call the Taymyr pathway, whose intensity pulsates but whose direction is nearly always the same—northward. The close relation between the Taymyr and return-flow pathways is shown in Figure 5.

The contrasts between the Taymyr pathway and the return-flow pathway are very important to Arctic air chemistry. Because the low-pressure areas pass completely by Bear Island, the return-flow pathway from Europe is only in place for 1-3 days before it is replaced with an entirely different kind of trajectory. As a result, the concentrations of pollutants in the Norwegian Arctic are "noisy," i.e., vary greatly and

with a rapid periodicity. But the Taymyr area has some of the least changeable winds in the Eurasian Arctic. As a result, concentrations of pollutants near Barrow are much ste.dier than at Bear Island, and have more of their variation associated with longer periodicities.

The meager precipitation in the interior of Asia during winter (nearly the lowest in the Northern Hemisphere), combined with the intensity and constancy of the winds along the Taymyr pathway, make it ideal for transporting pollution aerosol. Strong pollution sources in the central Soviet Union lie near the beginning of this path, and make it the dominant one for much of the Arctic, in particular for the North American Arctic.

(The scanty precipitation in the Arctic itself is one of the major reasons for Arctic haze. Because precipitation scavenges aerosol efficiently, regions of abundant precipitation have low concentrations of
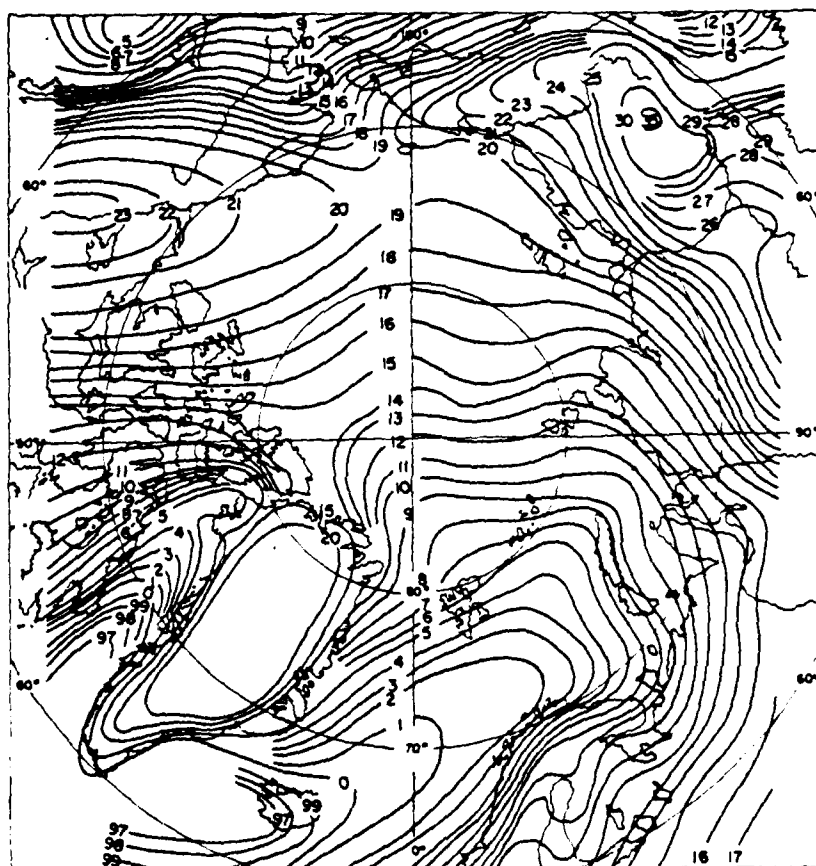

Figure 10. Mean surface pressure (mb) in January.[14][15]

aerosol. We feel that this is the reason why the seasonalities of aerosol and precipitation in the Arctic are inversely correlated.)

Because of its location, the Taymyr pathway is more difficult to verify by actual observation than is the return-flow pathway. We have been able to verify it to our satisfaction, though, with aerosol samples provided by the Air Force from routine Arctic flights. This has established that aerosol emerging from the Taymyr pathway matches the Barrow aerosol in composition, and is different from that of the Norwegian Arctic. Back-trajectories for the Taymyr samples, which are numerous enough to allow statistically valid conclusions to be drawn, pass through the central Soviet Union.

It is interesting to note that all the major pathways from Eurasia to the Arctic discussed above have one feature in common—the same migrating low-pressure areas. Because the importance of these lows to Arctic air chemistry has not been fully appreciated before, we summarize the above discussion by following the progress of a given low as it creates each of the pathways in turn.

Consider a low-pressure area fresh from the North American mainland. It first follows the North Atlantic storm track, which is basically the path of the Gulf Stream, i.e., from the Canadian Atlantic Provinces toward Iceland. As the low approaches Europe, it may combine with a high over Europe to produce a black episode into Scandinavia. The low then advances northward along the Norwegian coast. If conditions are right, it may extend the black episode to the Norwegian Arctic, where it would appear as a direct episode. As the low passes between Bear Island and Norway, on its way to Novaya Zemlya, it creates a brief, but strong, return-flow episode into the Norwegian Arctic. As it reaches Novaya Zemlya, the flow around the leading edge of the low combines with the Asiatic high to bring aerosol from the Soviet Union to the Arctic via the Taymyr pathway. By this time, the next low is already near Europe, and in a few days it will have arrived at Novaya Zemlya to replace the first one, which in the meantime has filled and disappeared. And so it goes throughout the winter, with successive pulses of aerosol to Scandinavia, the Norwegian Arctic, then the eastern Arctic, each type of pulse being a little slower and steadier than the one preceding it.

Movement of Pollution in the Arctic

Where does pollution aerosol go after it enters the Arctic? This depends on location and season. During early winter, from roughly November through January-February, the answers are very different for the Norwegian Arctic and for the Taymyr area. In the Norwegian Arctic, there is little tendency for deeper penetration into the Arctic, for the return-flow pathway is already heading south. At this time of year, aerosol from the Norwegian Arctic is not seen near Barrow. In the Taymyr area, however, air flows (in the mean) straight across the ice cap to the North American Arctic (see Figure 10). This penetration is facilitated by the lack of a high-pressure area over the pole at this time. This pressure pattern is at odds with the traditional picture of semi-permanent high pressure centered on the pole, and is a feature of Arctic meteorology whose importance to Arctic air chemistry has only recently been appreciated. Of course, not every pulse of air from the Taymyr flows to Barrow, but the distinct tendency is there, and each winter there are few events, typically of several days duration, that can be very strong. When the Asiatic high is well developed at the same time, the flow can come from deep inside the Soviet Union.

The situation during spring is quite different. By March and April, the classical polar high has formed, and is centered on the Alaskan side of the pole near the center of the pack ice (see Figure 11). This air mass blocks direct flow from the Taymyr to Alaska, and diverts it westward along the Eurasian coast into the Norwegian Arctic and thence past Greenland and along the Canadian Arctic Islands to Alaska. The portion of this pathway from the Norwegian Arctic is shown in idealized form in Figure 9. As far as the North American Arctic is concerned, the presence of the polar high favors nearer sources of aerosol along this path, i.e., Europe rather than the central Soviet Union. When conditions are right, (European) aerosol from the Norwegian Arctic can be transported *en masse* to Barrow. An example of this is given in Figure 12, which shows Mn and V in daily samples from Barrow during the winter of 1979-80. Throughout the early part of the winter, the Mn/V ratio remained between 1 and 2, i.e., near its winter-mean values. But in early March, aerosol with a Mn/V ratio of about 0.6 appeared suddenly and remained for nearly 6 weeks. Meteorological maps for this period revealed that there had been a prolonged direct episode northward from Europe beginning a few days before the new aerosol appeared at Barrow, and that there had been a strong polar high to divert the flow from the Norwegian Arctic toward Barrow. Because the low Mn/V ratios of this episode corresponded so closely to the winter mean at Bear Island (see Figure 7), there could be little doubt that this aerosol had, in fact, come from Europe, via the Norwegian Arctic. Events such as this seem to be a regular feature of spring
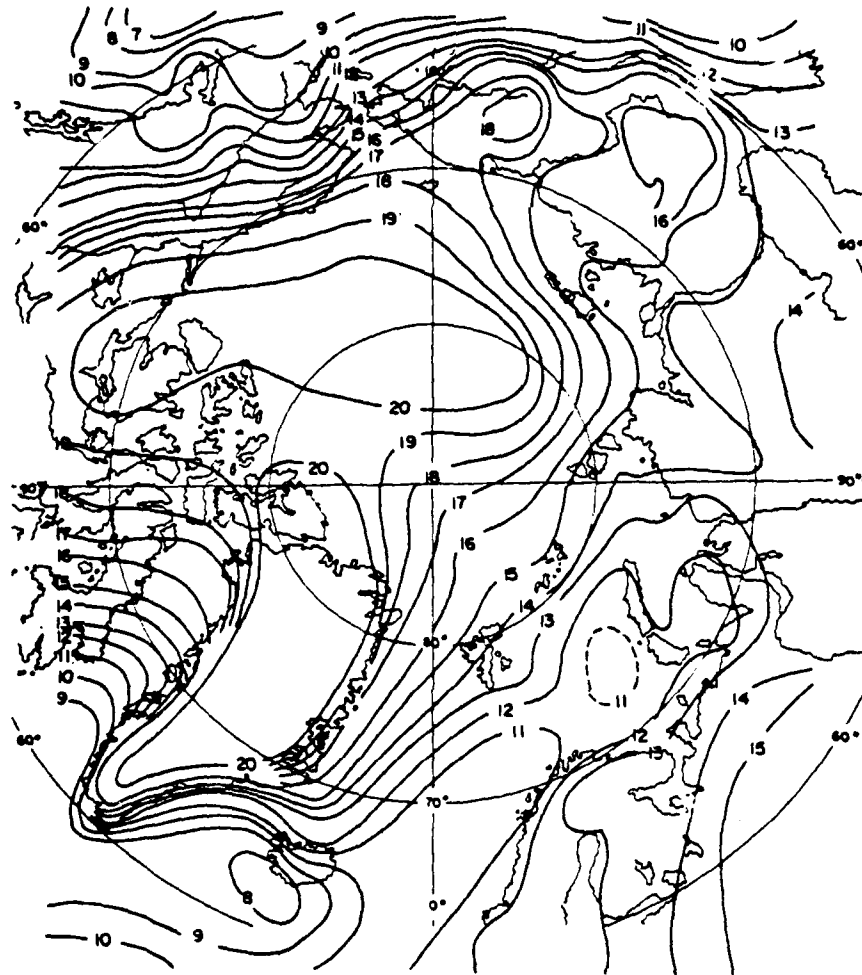
Figure 11. Mean surface pressure (mb) in April.[18,19]

at Barrow.

During March and April, the intensity of the general circulation decreases rapidly. Consequently, the migrating lows and the Asiatic high weaken, and transport to the Arctic declines rapidly. By May, nearly all the aerosol of winter is gone. The North American Arctic remains nearly free of pollution for the rest of the summer, until September or October when the cycle starts over again. On the Eurasian side, however, sources are nearer, and weak events of transport appear sporadically throughout the summer, but are curiosities rather than being of real significance. Between pulses, the air is extremely clean.

Altitude of Transport

One of the most interesting questions concerning transport of aerosol to the Arctic is its altitude. Long-range transport of aerosol is often regarded as occurring primarily in the mid-troposphere, where air moves faster and contaminants are removed more slowly than in the surface boundary layer below 1-2 km elevation. Transport aloft seems to be the rule for Saharan dust crossing the Atlantic, as well as for Asian desert dust over the Pacific Ocean. For this reason, it has been suggested at various times that long-range transport of pollution aerosol to the Arctic should take place well above the surface. While the last word is certainly not in on this subject, primarily because there have been so few measurements
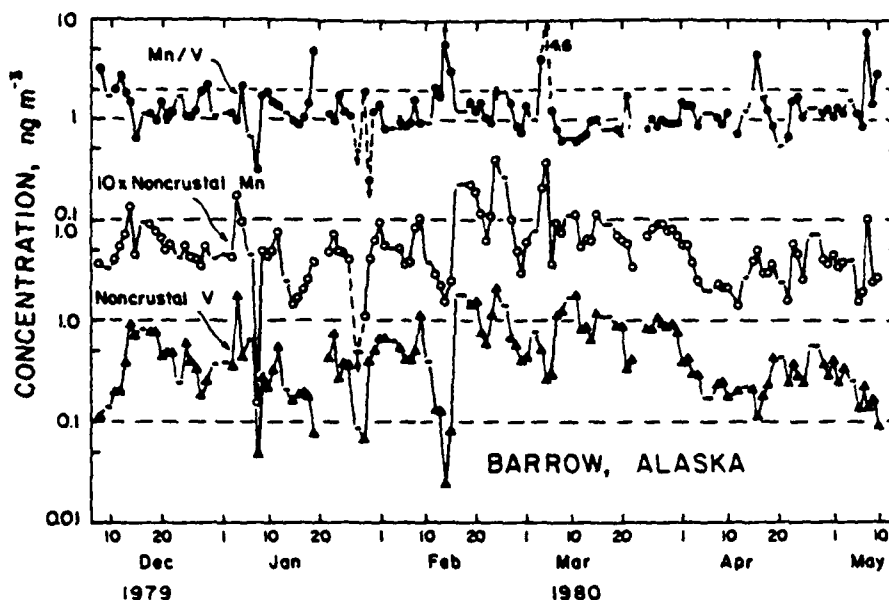
Figure 12. Noncrustal Mn, noncrustal V, and the Mn/V ratio in daily samples from
Barrow, Alaska, winter 1979-80.

aloft, the facts do not seem to support this supposition. Rather, the transport seems to be concentrated at unusually low altitudes, normally below 3 km (10,000 feet) and often at or below 1.5 km (5,000 feet). Because these observations "break all the rules" of long-range transport, they have been treated with considerable skepticism. But we have repeatedly found the haze at Barrow to be concentrated below 3 km or so. Although the Ptarmigan observers occasionally reported haze to the Arctic tropopause (8-9 km), the great majority of their sightings were below 5 km. (Lacking reference points in the upper troposphere, visual observations often overestimate the amount of haze.) Earlier balloon-based measurements of light scattering in the Alaskan Arctic by the University of Wyoming showed the bulk of the haze particles to be below 5 km. Various other aircraft measurements have suggested that the effective ceiling may be closer to 3 km.

There are good reasons why aerosol should be transported to the Arctic at lower elevations than elsewhere. The principal one is the lack of a driving force to lift the aerosol. The Arctic atmosphere is extremely stable during winter, when the ice cap is at its maximum and there is negligible direct solar radiation to destabilize the surface layer. The smooth surface of ice and snow minimizes mechanical turbulence as well. Low-pressure areas, which are a great destabilizing force in midlatitudes, are weak and in-

effective by the time they reach the Arctic. Nearer the sources there is also little tendency to mix aerosol aloft, for most of Eurasia is snow-covered during winter. In the central Soviet Union source area, temperatures are commonly −20°C and below. It should be remembered that the Eurasian population in general is located 10° farther north than is the North American population, and hence receives much less sunlight during winter. Even when aerosol is transported from central Europe to Scandinavia (50-60°N), it is held below 2 km altitude[4].

Thus, it would seem that transport to the Arctic takes place at lower elevations than is common in other parts of the world. One fortunate side effect of this low-level transport is that measurement at the surface, which is often the only practical way to accumulate regular samples, may be considerably more representative of the transport as a whole in the Arctic than in areas where the surface layer is cut off from transport aloft.

Environmental Effects of Arctic Haze

No discussion of Arctic haze would be complete without mention of its environmental effects, which may be classified as radiative, nucleational, or depositional. Radiative effects include scattering and absorption of visible light by the aerosol, and the conse-

quent alteration of the local radiation balance. In most aerosols scattering dominates absorption, and Arctic haze is no exception. Sulfate and the associated water are the major scatterers. Other than creating the visible haze, however, scattering is a relatively unimportant feature of the Arctic aerosol; it merely lengthens the path of the light rays as they pass through the Arctic atmosphere. Absorption is far more important, in spite of its smaller magnitude. The primary absorber in most aerosols, and in the Arctic aerosol as well, is black carbon, or soot. Arctic haze contains much more black carbon than expected—orders of magnitude more than found over the Pacific Ocean, for example, and 2-3 times more than predicted based on pollutants such as sulfate, vanadium or manganese. Measurements by Dr. Edward M. Patterson of the Georgia Institute of Technology show that carbon is higher in concentration at Barrow than at Bear Island. We are tentatively ascribing these high concentrations to some feature of air pollution in the central Soviet Union source area that we do not understand. It may be from a general lack of pollution controls there, from the predominant use of coal as an energy source, or it may have some entirely different explanation.

Whatever the reason, there is a great deal of carbon in the aerosol of the North American Arctic. It has been estimated that during spring, this carbon can heat the local lower atmosphere by as much as 1 °C per day[19]. More recent estimates have tended to revise this figure downward, but it still remains unexpectedly high relative to the nature of the area. This topic is currently undergoing extensive further study, because any effect of man that tends to heat the polar regions is well worth monitoring closely.

Another aspect of Arctic carbon is its deposition onto the pack ice, where is continues to absorb solar radiation throughout the summer, long after atmospheric carbon has disappeared[20,21]. Clearly, this can greatly extend the influence on Arctic climate and preliminary evidence indicates that carbon in Arctic snow can indeed increase the latter's absorption of visible radiation by several percent[21].

The nucleational aspect of Arctic haze may be one of its most important environmental effects. In general, three kinds of nuclei are recognized: condensation nuclei (CN), such as are measured by an Aitken counter at several hundred percent supersaturation; cloud-condensation nuclei (CCN), particles which nucleate water at the much lower supersaturations actually found in clouds (a few tenths of a percent); and ice nuclei (IN), particles which nucleate ice crystals in clouds. CN counts give the total numbers of particles in the atmosphere, rather than information on their nucleational properties, and hence will not be considered further here. CCN and IN are environmentally meaningful quantities, and are presently the subject of a Ph.D. thesis by Mr. Randolph D. Borys of Colorado State University (under ONR sponsorship). His preliminary data are most interesting—they show that Arctic haze increases the numbers of CCN but seems to decrease the numbers of IN. The increase of CCN is tentatively linked to elevated sulfate concentrations in Arctic haze, whereas the decrease of IN concentrations is more puzzling. One proposal is that the surfaces of IN (often soil or mineral particles) may be poisoned by secondary material such as sulfate or organics deposited during transport. In one completed study by Mr. Borys, an episode of aerosol transport from Europe to Iceland was observed in August 1979. During this event, concentrations of both CCN and pollution aerosol were temporarily elevated[22].

Depositional effects of Arctic aerosol have not been studied as much as its radiative and nucleational effects have. Carbon deposited on pack ice has already been mentioned. But many other elements and ions can be detected in Arctic snows; the relation between the trace compositions of snows and parent aerosol is not at all clear, however, and may be very complex. In one now-classic case, trace elements in a series of snow samples near Barrow were measured; from their ratios, it was concluded that the aerosol near Barrow was primarily natural in origin[23]. But these same elements in the Barrow aerosol reveal an overwhelming anthropogenic influence. Part of this discrepancy may be from the methods used to interpret the snow data, but part of it may also be due to selective scavenging of aerosol by snow. This aerosol-snow dichotomy is worthy of considerable further study, for it is central to the interpretation of trace-element data from the Greenland Ice Sheet, which are used to derive historical trends of air pollution in the Northern Hemisphere.

Ecological aspects of deposition to the surface of the Arctic may also be important. It has recently been calculated that more lead enters the Arctic Ocean from the atmosphere than from the influx of North Atlantic water or from rivers[24]. The situation may well be the same for other metals of ecological interest. These metals and other substances such as organic compounds are also deposited on the tundra, where they enter the Arctic food chain. The ramifications of this remain completely unexplored. The Arctic aerosol is also very acidic, particularly during spring. The effects of this acidity on the tundra biome need to be investigated.

Further Studies—International Cooperation

The ONR Arctic haze project has stimulated the creation of several other programs: The Canadian Atmospheric Environment Service is now operating three sampling stations in the Canadian Arctic, at Mould Bay, Igloolik, and Alert. Denmark has five sampling sites around the perimeter of Greenland. Iceland is engaged in a long-term cooperative study of their aerosol with URI. The winter and summer aerosol of western Ireland was studied with the aid of University College, Galway. The Norwegian Institute for Air Research has conducted several years of air sampling at both Bear Island and Spitsbergen, and is about to expand its program during the next five years. One of the major scientific goals of the summer 1980 Arctic expedition of the Swedish icebreaker *Ymer* was an international study of air pollution in the Norwegian Arctic. As a result of the *Ymer* cruise, the Johannes Gutenberg University in Mainz, W. Germany has begun its own study of the Arctic aerosol.

Several countries and laboratories interested in Arctic air pollution have formed the Arctic Air-Sampling Network[35]. From its inception in 1977 (at a meeting sponsored by ONR), the network has grown until it now includes approximately 15 sampling sites. Figure 13 shows the locations of these sites as of 1980.

Two international conferences have been held on Arctic air chemistry, the first at Oslo in April 1977 and the second at Rhode Island in May 1980. The proceedings of the Rhode Island symposium comprised the August 1981 issue of the international journal *Atmospheric Environment*. A third conference is tentatively scheduled for October 1983 in Toronto.

The current surge of interest in Arctic air pollution has caused the GMCC Program to upgrade its activities at Barrow. Of its four baseline observatories, Barrow now receives the most attention. Last spring, GMCC sponsored a special series of accelerated measurements there, aimed primarily at further documenting the radiative aspects of Arctic haze.

Without a doubt, the greatest disappointment in our six-year term with Arctic haze was our failure to induce the Soviet Union to participate. Repeated overtures have been made to various individuals and departments, all without success. This is most unfortunate in light of the evidence for the central Soviet Union as the major source of aerosol to the North American Arctic.
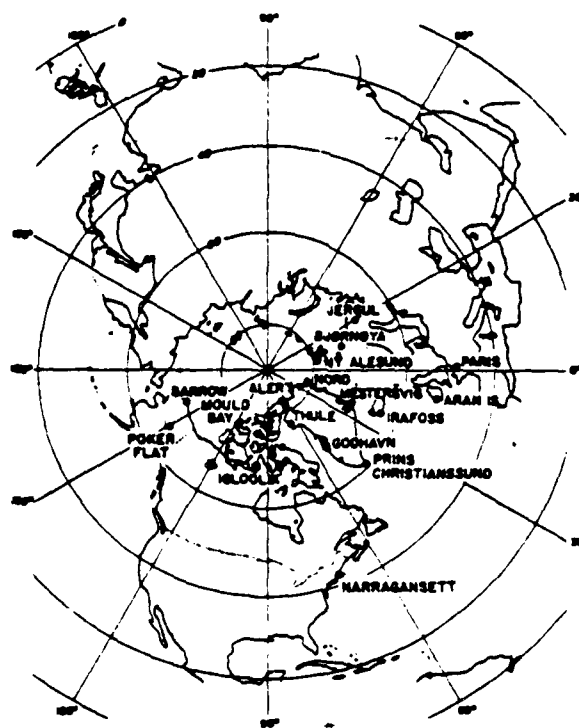
Figure 13. Sites of the Arctic Air-Sampling Network in 1980.[35]

Broader Outgrowths of This Research

There have been important spinoffs into other areas from the ONR Arctic Haze Program. One of these is the development of a general system of elemental tracers for source areas of pollution aerosol, which is sure to find application in various regions and atmospheric problems. This system is still in its infancy. A major effort to develop it into a full-fledged system involving many tracer elements is now under way at URI for Europe, via a collection of cooperative local efforts called the European Aerosol-Sampling Network. Aerosol samples are being collected in Belgium, West Germany, Austria, Hungary, Sweden, Finland, and eventually also Poland, we hope, and are sent to the University of Rhode Island for analysis. Compositional patterns over Europe will be correlated with similar observations on both sides of the Arctic; from these correlations, we hope to be able to deduce which elements make the best tracers, and which subregions of Europe are the most important sources of Arctic aerosol. From this, it should be possible to go more deeply into meteorological aspects of transport to the Arctic.

Another major spinoff, just developing, is the

construction of a similar set of elemental tracers for the eastern United States and its application to the problem of sources and transport of acidity to the Northeast. This project is particularly noteworthy because acid precipitation is the number-one environmental issue in the United States today. The sources of acid rain in the Northeast are not at all clear; it is our hope that the tracer techniques first developed for the Arctic can be expanded and refined for the Northeast, and will shed some light on the true sources of acid rain there.

In conclusion, the ONR-sponsored research of the last six years on Arctic haze has shown that it is strongly pollution-derived, that its sources are primarily Eurasian but differ from one part of the Arctic to another, that it is transported in the lower troposphere by major synoptic systems, primarily the migratory lows and the polar high, and that it may have important radiative, nucleational and depositional effects. These conclusions are only broad generalizations, however—much work remains to be done providing details for each area. In the future, we hope to use elemental tracers to delineate the sources more precisely, to develop more appropriate meteorological techniques to better understand the transport, to fill in the third dimension with more aircraft-based observations, and to look further into the various environmental effects. We hope to continue to stimulate other groups to join us, in order to broaden the range of studies. But one thing is sure:

no matter what the total effort devoted to Arctic haze, and no matter what the eventual mix of laboratories and projects involved, the study of air pollution in this area will continue to be fascinating and stimulating.

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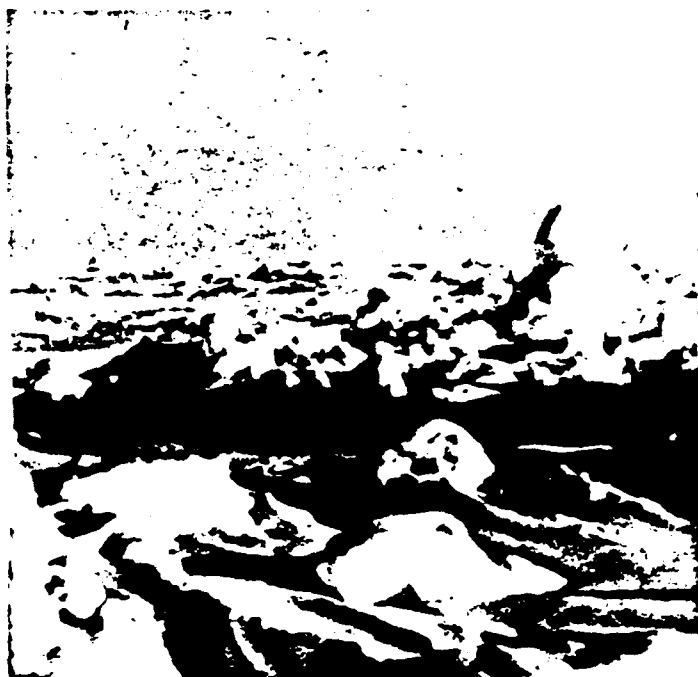
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E.5.

ELEMENTAL TRACERS OF DISTANT REGIONAL

POLLUTION AEROSOLS

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Summary

A seven-element tracer system has revealed that regional pollution aerosols of both North America and Europe have discrete and different signatures that can be followed into remote areas up to several thousand km downwind. In aerosols of mixed origin, regional contributions to the tracer elements can be resolved by least-squares procedures. After transport of several hundred km, secondary sulfate can also be apportioned satisfactorily. Regional elemental tracers thus offer a way to determine the sources of pollution aerosol in important areas such as the northeastern United States, Scandinavia, and the Arctic, where it is otherwise presently impossible.

Need for regional tracers

The routine transport of pollution aerosol long distances through the atmosphere is increasingly recognized as an important aspect of atmospheric science. Once considered a rarity, atmospheric transport on the scale of 1,000-10,000 km is now invoked regularly to understand the results of aerosol studies in rural and remote areas (1).

But long-range transport has created a whole new set of interpretive problems. While it is relatively easy to identify the part of the aerosol which has been transported, it is often difficult or impossible to pinpoint its source area(s). (At distances of a few hundred km or more, source areas are normally much more important than point sources.)

Sheer distance can cause problems. For example, it has been extremely difficult to decide whether the important sources of pollution aerosol observed at Barrow Alaska are located in North America, Europe or Asia. With air-mass trajectories from these sources being 5,000-10,000 km or more in length and representing travel times of 5-10 days or more, pure meteorological techniques have not led to a consensus about even the continent(s) of origin, much less any particular regions within the continent(s) (2).

The configuration of sources can also make identification difficult. In the northeastern United States, for example, where the source areas of acid aerosol and precipitation are currently in dispute, distances of transport are much shorter (1,000 km or less) but the demography is complex. As a result, trajectories to areas of concern such as the Adirondacks often pass over several strong source areas in their last few hundred km. No available transport model can reliably apportion the contributions of these sources to the final sulfate, acidity or other ubiquitous constituents of the aerosol.

There is thus a great need for a more direct way to identify distant sources of pollution aerosol. Such a capability would be of practical as well as scientific importance, because it could be extended ultimately to determining source areas of acid precipitation. It may cost as much as $20-100 billion to reduce emissions of sulfur dioxide in the eastern United States over the next decade; controlling the wrong sources would be a very costly error indeed.

We feel that chemical tracers in the aerosol itself hold considerable promise. This article deals with our efforts on regional elemental tracers; eventually, organic and stable isotopic tracers can probably be developed and used analogously.

Prospects for regional elemental tracers

Pollution aerosol contains all elements: no true tracers, or elements unique to specific source areas, exist. But it is reasonable to expect the proportions of at least some elements to vary with source area because different areas have different mixes of the major aerosol sources (combustion, industry, transportation, etc.), different mixes of fuels, fuels from different origins, different industrial bases, and different degrees of pollution control. A priori, however, the number of regional elemental signatures, the magnitude of their differences, and the elements involved cannot be predicted; they must be determined empirically.

In general, regional tracers are constructed and used quite differently from urban tracers. Elemental signatures used to deduce the sources of urban aerosol by receptor-oriented techniques (3) are usually derived for either point sources or specific types of sources (automotive exhaust, for example). Regional aerosols, by contrast, are mixes of many sources and should thus resemble one another much more than signatures within an urban

region should. The similarities among pollution aerosols have been recognized for years (4), to the point that many have doubted whether useful regional differences could ever be found. We have determined, though, that discrete regional signatures do indeed exist, and are commonly very different from one another.

The two keys to deriving regional signatures are finding the right elements and handling the data with the appropriate statistical techniques. The "marker-element" approach often used in urban studies (where the contribution of a source is evaluated by a single element) cannot be used with regional signatures because of their great similarities; the inclusion of all available elements in signatures, as practiced in some urban studies, goes to the other extreme and adds too much noise to regional signatures. The best approach seems to be a compromise--limit regional signatures to those few elements with the greatest tracer power.

Several requirements should be met by elements and signatures before they can be used in a regional tracer system: the elements should be pollution-derived, sampled and measured accurately, emitted stably and homogeneously in each region, and present on particles small enough to be transported long distances; each signature should remain recognizable during transport. Our preliminary assessment indicates that all these requirements are met adequately; we illustrate several of them in the discussion that follows. Nevertheless, some of these requirements, such as conservation of proportions during transport, are sufficiently critical that we have built a system of routine checks into our operating system.

A seven-element tracer system

The first regional tracer was the noncrustal Mn/V ratio (5). This tracer was designed to determine whether Arctic aerosol originated mainly

from Europe or eastern North America. Although the noncrustal Mn/V ratio succeeded in doing this, its greatest contribution ` s to demon- strate the general feasibility of regional elemental tracers, and hence to stimulate the development of more sophisticated tracing systems. At present, we are using a seven-element tracer system involving As, Sb, Se, Zn, In, noncrustal Mn and noncrustal V. The design of this system and several of its applications are discussed below. No tracer system is per- fect; this one is sure to be modified in the future.

These seven elements were chosen from the 40-45 that we measure by neutron activation as best meeting the criteria of being pollution-derived. fine-particle and accurately analyzable. Potential tracers rejected for analytical reasons included Cu, Ni, Ga, Mo, Ag, Cd, Sn, W, Au and Hg. With better analysis, any or all of these might be included in the system. Lead and elemental carbon are strong candidates which should also be in- vestigated. Indium (In), whose analysis is poorer than those of the other six elements, was retained because of its great utility in tracing smelters (6).

Our regional signatures consist of six elemental ratios to Se. Ratios are used to normalize for variable meteorological effects such as dispersion and removal; Se is used in the denominator because it is a general pollut- ant found at similar concentrations in diverse source areas, and hence will not bias the ratios toward any particular region. Other general pollution elements such as Pb or C might also be used in the denominator.

The signature of a source region cannot be derived in a completely straightforward fashion because most regions can be affected by aerosols from other regions. To eliminate such interference, we are developing a protocol which involves multiple samples at multiple sites inside and

outside the region. At each site, at least 100 (ideally) daily samples
are taken and analyzed for the tracer elements. Logarithmic frequency
distributions of the various X/Se ratios are then constructed and exa-
mined for the presence of modes, or maxima, which represent characteris-
tic aerosols for the sites. The meteorological and chemical characteris-
tics of the samples in a mode usually give a good idea of its source. By
combining the modal information from several sites in a region, its aero-
sol may be distinguished from those of neighboring regions with greater
certainty. As a final check, regional signatures are verified by sampling
downwind of the region. This also reveals whether any elemental ratios
change significantly during transport.

To date, we have used filter samples of total aerosol exclusively
(and successfully) for our tracer system. In effect, this provides size-
segregated data because the tracer elements chosen are mostly submicron.
True fine-particle samples would probably improve the tracer system by
reducing the variability of elemental ratios and allowing mixed-mode ele-
ments such as Fe, Co and Cr to be considered. But the degree of improve-
ment is not yet known, and must be considered in light of the facts that
size-segregated samples are smaller and not readily available from many
regions of interest. Size-segregated samples may be desirable, but they
are certainly not necessary at present.

Factor analysis and cluster analysis, while useful for understanding
broad elemental relationships and the general pollution character of a
site, have not been particularly successful in selecting elements or de-
fining signatures. The reason for this seems to be that both these tech-
niques, as well as all others which are based on single measures of simi-
larity between elements in a collection of samples, do not adequately

reveal the complex relationships implicit in multi-modal frequency distributions.

Regional signatures in North America, Europe and the Arctic

Figure 1 shows the six X/Se distributions for six sites at which we have reasonable amounts of data: Narragansett, Rhode Island and Underhill, Vermont (eastern North America); Kecskemét, Hungary and Rörvik, Sweden (Europe); and Barrow, Alaska and Bear Island, Norway (Arctic) (7). Depending on element and location, 1-4 modes are seen in each distribution. The modes are reasonably symmetric (i.e., log-normal), with geometric standard deviations of 1.4-1.6 (68% of the points found within a total factor of 2-3). Some modes have geometric standard deviations as low as 1.2.

More types of aerosol may be present at a site than suggested by the major modes. Broader-than-normal modes may be composed of two or more unresolved modes, as seems often to be the case for Zn/Se and Sb/Se, for example. Small features may represent infrequent appearances of aerosols which are more important elsewhere. An example of this is the small upper mode of As/Se at Rörvik (ratios of 8-10), which coincides with the principal mode (6-12) at Kecskemét (we show below that the upper mode at Rorvik was created by a pulse of aerosol from eastern Europe). Another example is the lower shoulder of Zn/Se at Narragansett (ratios of 10-20), which has been resolved into a discrete mode by subsequent shorter-period samples. The real number of modes in most distributions is still unknown, and may be considerably larger than the number apparent from Figure 1.

The membership in most modes is organized, that is, samples in a certain mode of one distribution are usually found together in other distributions. For example, the samples from Eastern Europe which comprise the upper As/Se mode at Rörvik also comprise the low shoulder of

noncrustal V/Se there (ratios of 3-6). This illustrates that discrete
aerosols with reproducible signatures do indeed exist. As demonstrated
below, they can usually be identified with well-defined geographical
source areas.

We are presently working with 12 regional signatures derived from
the modes of Figure 1 and their raw data. These signatures, six of which
are from North America and six of which are from Europe, are shown in
Table 1. The signature of regional New England (NE) was derived from
four daily samples at Underhill (4-7 August 1982), in aged Canadian air
masses which had not been affected by the large nonferrous smelters of
the Sudbury Basin. The outstanding feature of this signature is its low
As/Se ratio, which we interpret to mean minimal coal influence. We have
also detected this signature in Narragansett and South Portland, Maine
(the small low-As mode at Narragansett in Figure 1 is associated with this
kind of aerosol). The "Boston" aerosol (BOS) was derived from three daily
samples at Narragansett when the winds came from the direction of Boston
and Providence and SO_2 concentrations were high (20 July, 3, 6 August 1982).
The New York City signature (NYC) came from six semi-weekly samples taken
in midtown Manhattan during winter 1977-78. In order to better apply this
signature to summer samples elsewhere, we have reduced its noncrustal V
by 50% (8). To better simulate the regional signature near New York, we
have reduced the Zn, which is abnormally enriched in urban aerosol, by
30% (because 30% of the Zn is coarse-particle, and presumably local, not
regional, there). The Washington, D.C. signature (WASH) came from grand
averages of individual average concentrations for 10 sites in the Washing-
ton area during August and September 1976 (9). As in New York, Zn was
reduced by 30% in an attempt to represent aerosol from the central mid-

Atlantic states. The Midwest coal signature (MWC) was derived from four daily samples in Underhill, Vermont in July 1982, when an unusually strong signal of coal was present and associated with winds from the S-SW. This signature does not represent pure coal emissions, of course, but rather an area where coal emissions are unusually strong. The Canadian smelter signal (SONT) was derived from three samples in southern Ontario roughly 300 km ESE of Sudbury (10). It is enriched in As and In. (The small groups of samples defining the signatures were representative distillations of larger sets of data; the numbers of samples in each group were kept comparable for statistical purposes.)

The samples from Kecskemét and Rörvik have allowed us to construct six regional signatures for Europe, three from the East and three from the West. Signature EEURH came from 4 samples associated with the most prominent mode of As/Se in Kecskemét. Signature EEURS came from three samples at Rörvik during the most intense "black episode" (11) of the last decade. As shown in Table 2, this aerosol was very different from that before and after the episode, and had eastern European rather than western European characteristics. These samples made up most of the small upper mode of As/Se at Rörvik shown in Figure 1. Signature EEURF came from four samples at Ähtäri, southern Finland, during the same black episode. Table 2 also shows these samples and how they closely resembled aerosol at Rörvik during the same period. The two signatures of western Europe, WEURS and WEURH, were derived from 5 samples at Rörvik when the winds were from the SW and 5 samples at Kecskemét when the winds were from the west, respectively. For at least As/Se and noncrustal V/Se, these samples appeared in well-defined modes at the two sites. The last European signature is of Scandinavia (SCANS), as determined from periods

of unusually high noncrustal V/Se at Rörvik, which usually coincided
with weak circulation or winds from the north.

The western and eastern European signatures confirm the existence
of general regional aerosols which appear at various sites in and around
large source regions. Because the three eastern signatures are so simi-
lar, they can be combined into a general eastern European signature (EEUR),
as shown in Table 1. Similarly, the two western European signatures can
be combined into the general WEUR. As more data become available from
eastern North America, it should be possible to construct general signa-
tures there as well. For illustrative purposes we have combined the four
coastal signatures NE, BOS, NYC and WASH into ECOAST, which is also shown
in Table 1. (For later use, all samples from North America and Europe
were combined to form the continental signatures NAMER and EUR.) Note
that the principal modes of As/Se, noncrustal V/Se and Zn/Se at Barrow
and Bear Island agree quite well with the WEUR and EEUR modes at Rörvik
and Kecskemét.

Some of the most significant features emerging for elemental tracers
are that the tracing power varies widely from element to element, that
the majority of the tracing power is vested in only a very few elements,
and that the discriminatory power of an element, as measured by the range
of its X/Se ratio and its degree of modality, is similar at widely diverse
sites. For example, As/Se and Zn/Se, have, respectively, large ranges with
well-defined multiple modes and small ranges with single modes at most
sites. Thus, some elements are inherently much better tracers than others.
The reasons for this, although not yet fully understood, are probably geo-
chemical. They may well be related to large-scale elemental variations
in the earth's crust.

Table 3 illustrates two ways to measure the relative discrimina-
tory power of tracer elements. In the first, linear discriminant analy-
sis was used to classify the 48 signatures of Table 1 into the twelve,
six and two groups shown in Table 3. Initially, all six of our X/Se
ratios were used. Then the samples were reclassified with each of the
ratios removed in turn. The greater the discriminatory power of a ratio,
the more samples will be misclassified when it is removed. The results
showed that As/Se and noncrustal V/Se had the greatest discriminatory
power, Zn/Se had somewhat less power, and that the other three ratios
contributed little or nothing on the average. When both As/Se and non-
crustal V/Se were removed, the extent of misclassification became greater
than their summed individual effects. As a more sophisticated test of
discriminatory power, stepwise discriminant analysis (13) was applied to
the six ratios as they were used to segregate the 48 samples into groups
of twelve, six and two signatures. The results are shown at the bottom
of Table 3. As/Se and noncrustal V/Se were the only two ratios possessing
good tracer power in all three cases. We suspect that these results are
general for North America and Eurasia.

In an effort to improve the discriminatory power of our ratios, we
are presently investigating the possibility of using quadratic discrimi-
nant analysis, where elemental ratios are replaced by higher-order terms.
The discriminatory power of optimized quadratic functions of ratios seems
to be at least 20-40% greater than that of linear functions. Products
involving As/Se and noncrustal V/Se are the most useful.

Empirical confirmation that certain elements are crucial to a succes-
ful regional tracer system comes from comparing our experience in southern
Sweden with that of Lannefors et al. (14), who took daily aerosol samples

for one year at Sjöängen, only 200 km NE of Rörvik. Their data, which contained S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br and Pb but lacked As, Se, Sb and In, were unable to differentiate between aerosol from eastern and western Europe.

Recall that our seven-element tracer system was based on elements which were pollution-derived, fine-particle, and determined well by neutron activation. To test whether these criteria were unduly restrictive, we have investigated the tracer power of nine additional elements (Al, Sc, Cr, Co, Fe, La, Ce, Sm, Th) by means of stepwise discriminant analysis on the same 48 signature samples. These elements are as well determined as the seven basic tracers, but are mostly coarse-particle in the aerosol (Cr, Co and Fe usually have a fine-particle component, and La and Ce occasionally do). In general, the tracer power of La, Ce and Sc was comparable to or better than that of Sb, In and noncrustal Mn but less than that of As, noncrustal V and Zn. Al, Sm and Th appeared to have little promise as tracers. Fe, Co and Cr behaved in an intermediate fashion. At this time, it is not known how the apparent tracer power of La, Ce and Sc is partitioned between coarse- and fine-particle components. That fraction associated with coarse aerosol may be less useful than suggested by these signature samples, because coarse aerosol is not transported as efficiently as fine aerosol is.

Use of regional signatures to classify unknown samples

Once discriminant analysis has been used to determine classification criteria from samples with distinctive signatures, one may then classify other, nonsignature samples (i.e., not used to determine a signature) into those groups. In the ultimate case, the origin of an aerosol sample could be determined "blind", that is, from its chemical composition alone. We

have not yet achieved this ideal, nor are we sure that it will ever be possible or even necessary.

Table 4 illustrates the present status of geographical classification of unknown samples by our seven-element tracer system. In the upper part of the table, nonsignature samples from Narragansett, Underhill, Rörvik and Kecskemét have been classified as North American or European based first on twelve individual signatures, then on six regional signatures, and finally on the two continental signatures of Table 1. All samples from Kecskemét were always classified correctly (to Europe). At Narragansett, 90-95% were classified correctly (to North America). At Underhill and Rörvik, however, only 60-80% were classified correctly. Very similar results were obtained when the noncrustal Mn/Se and In/Se ratios were eliminated. Classifying samples by continent is a severe test, however, because it is much more difficult for entire continents to have distinctive signatures than it is for smaller regions.

The center of Table 4 shows how samples at Bear Island and Barrow were classified relative to the five most appropriate regional signatures (SCANS, WEUR, EEUR, ECOAST, MWC). Only 1 out of 32 (3%) and 5 out of 33 (15%), respectively, were called North American. This confirms our earlier conclusions, reached independently, that Arctic pollution aerosol is strongly Eurasian in origin (15). As high-quality signatures for the Soviet Union become available, the number of cases of Arctic aerosol classified as North American will probably decline even further.

The bottom of Table 4 illustrates how the nonsignature samples at Narragansett and Underhill were classified relative to the six North American signatures. At Narragansett, the four coastal signatures accounted for three-quarters of the cases, with the other quarter coming

from the interior coal signature. This result is striking, for it con-
firms in a multi-elemental sense the conclusions about dominance of coastal
aerosol reached earlier by noncrustal Mn and V alone (8). At Underhill, on
the other hand, the most common signature is New England, (40%) followed by
other East Coast (30%) and interior coal (25%). Considering Underhill's
location in northern New England, this distribution of sources is highly
reasonable.

Apportionment of tracer elements among regional sources

Discriminant analysis determines which of several signatures is most
likely to account for an aerosol sample. In actuality, however, most aero-
sol samples come from more than one source, either because of the history
of the air mass or because of changes of air mass during sampling. Using
least-squares techniques, the abundances of the seven tracer elements in
a sample can be apportioned among the various regional aerosols which may
have contributed to it (16). Table 6 illustrates one such apportionment
for an August 1979 aerosol sample from Narragansett, using the elemental
concentrations of the five regional aerosols listed in Table 5 (17). In
this sample, the abundances of six of the seven tracer elements were ac-
counted for to better than 20% by four of the signatures (NYC gave a nega-
tive coefficient, so it was eliminated and the regression was rerun with
four sources). The weighting factor shown on the left is really two fac-
tors, one to scale the numerical values of the different elements and
another to weight As, Se, noncrustal V and Zn relative to Sb, In and non-
crustal Mn. (The final apportionment is insensitive to weighting factor,
however.) Note that about one-half the As and Se were associated with the
interior coal signal, whereas 60-80% of the Sb, Zn, In and noncrustal Mn
and more than 90% of the noncrustal V came from the coastal source. This
type of result is common for Narragansett during summer.

Table 7 summarizes the apportionments of 14 consecutive semi-weekly samples from Narragansett during summer 1979, and shows that the mix of sources can vary strongly in response to large-scale meteorology. During summer 1979, Narragansett had two major sulfate episodes, one in July and one in August. The first was a "typical" summer episode, with winds from the S-W. The second episode was different, however. It had the highest summer sulfate seen to that time in Narragansett, but the lowest (most northeastern) noncrustal Mn/V ratios and the lowest As. Meteorological maps showed this latter episode to have been the product of large-scale stagnation in the Northeast of air which had originated largely in the upper Great Lakes and Canada. In other words, the first episode appeared to be mid-Atlantic and/or midwestern in origin, whereas the second appeared to be more New England/Canadian.

The apportionments bore out these observations. The first episode had high regression coefficients from the Midwest, normal coefficients from Boston, and low coefficients from New England. The second episode, by contrast, had coefficients of 0.0 from the Midwest combined with normal-to-high coefficients from Boston and New England. Washington aerosol was negligible throughout the period; contributions from the New York area were low-to-moderate and irregular.

Regional apportionment of sulfate

Although our tracer system is based on primary pollution elements, i.e., those emitted directly as aerosol, one of its most important uses will be to understand the regional origins of secondary species, such as sulfate and acidity, which are formed in the atmosphere from primary precursors. Sulfate is the most abundant constituent of many remote aerosols; both sulfate and acidity are of great concern in acid deposition.

Strictly speaking, primary constituents cannot trace secondary con-
stituents. Near strong sources of (primary) aerosol, such as in large
urban or industrial areas, our tracer system should work poorly for sul-
fate. Outside urban/industrial areas, however, where regional aerosols
dominate, a primary tracer system should work better, although there may
still be difficulties. In remote areas, primary tracers should work still
better, because most of the primary precursors such as SO_2 will have been
converted or otherwise removed, i.e., the secondary species will have
reached quasi-stable proportions. Under these conditions, the aged re-
gional aerosols would effectively contain a sulfate component linked to
the primary signature elements.

This appears to be the situation at Underhill, Vermont, for example.
In a series of 39 daily samples from July and August 1982, we have deter-
mined the "effective" sulfate in the various regional signatures by first
apportioning the seven tracer elements, then regressing the sulfate of
each sample against the regional coefficients derived for that sample.
The results gave the collowing approximate concentrations of sulfate:
21 ± 1 μg m^{-3} for the interior coal signature (MWC), 7 ± 3 μg m^{-3} for the mid-
Atlantic region (WASH) and 3 ± 1 μg m^{-3} for the local aerosol (NE). Based
on these values, the predicted sulfate concentrations generally reproduced
the observed values to within 25% or so (Figure 2). This accuracy is
comparable to that obtained for the primary tracer elements. In particu-
lar, each of the peaks and valleys of sulfate was predicted.

At Narragansett, Rhode Island, however, the same approach gave dis-
tinctly poorer results. Figure 2 shows the observed and predicted sulfate
for 21 semi-weekly samples during June-September 1979. The fractional
errors were twice as large as at Underhill, neither peaks nor valleys

were predicted correctly, and a period of low sulfate at the beginning
was missed entirely. This behavior is consistent with Narragansett's
less remote location and with the abundant SO_2 observed there even during
summer (2-20 μg m^{-3}) (18). The "noise" in sulfate at Narragansett most
likely results from variable and unpredictable oxidation of this sub-
regional SO_2, on a scale too small to be seen at Underhill. This com-
plexity is borne out by time traces of the elements at Narragansett, which
are considerably more irregular relative to each other and to sulfate than
at Underhill. Thus, it would appear that both primary and seconday aero-
sol of the coastal Northeast are more local in origin than in northern
New England. Control of this aerosol and its deposition will require
different strategies for different parts of the Northeast.

The future

In spite of the successes given above, the exploitation of regional
tracers of pollution aerosol is still new. Almost every aspect of the
procedure is sure to be improved. Particular benefits, though, will come
from attention to a few key areas: systematic search for additional ele-
ments with high tracer potential, tests of the gains from significantly
increased numbers of samples per site and per signature, evaluation of the
utility of size-segregated sampling, refinement of ways to trace secon-
dary species, and additional exploratory applications to aerosol of remote
areas. Incorporating organic compounds and stable isotopes into signa-
tures also has great potential. Lastly, the application of regional
tracers to precipitation would seem to be a logical extension of high
priority.

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    Underhill samples taken daily during July-August 1982; 76
    Rörvik samples taken for 1-3 days each during fall and winter
    1981-82; 31 Kecskemét samples taken daily during fall-winter
    1981-82; 66 Bear Island samples taken for 2-3 days each during
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12. Linear discriminant analysis is a statistical technique used to define groups of observations with known attributes and then classify other observations into one of these groups. See D.F. Morrison, _Multivariate Statistical Methods_ (McGraw-Hill, New York, 1976), pp. 230-246. For linear discriminant analysis, we use a program in SAS-79, SAS Institute Inc., Cary, NC.

13. In stepwise discriminant analysis, variables are added to the discriminant function in the order that they enhance the separation between groups. For stepwise discriminant analysis, we use a program in BMDP, Biomedical Computer Programs, P-Series, 1979, Univ. of Calif. Press.

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16. For least-squares apportionments of aerosol we use the program PETMIX, originally developed for petrologic studies. [T.L. Wright and P.C. Doherty, _GSA Bull_. _81_, 1995(1970)], and a program in SAS-79, SAS Institute, Inc., Cary, NC.

17. Tables 5-7 from K.A. Rahn and D.H. Lowenthal paper presented at the 17th Annual Conference on Trace Substances in Environmental Health, Columbia Missouri, 13-16 June 1983, to appear in Proceedings.

18. T.R. Fogg, personal communication.

Figure 1.   Frequency distributions of six elemental ratios at
            six sites in eastern North America, Europe and the
            Arctic.
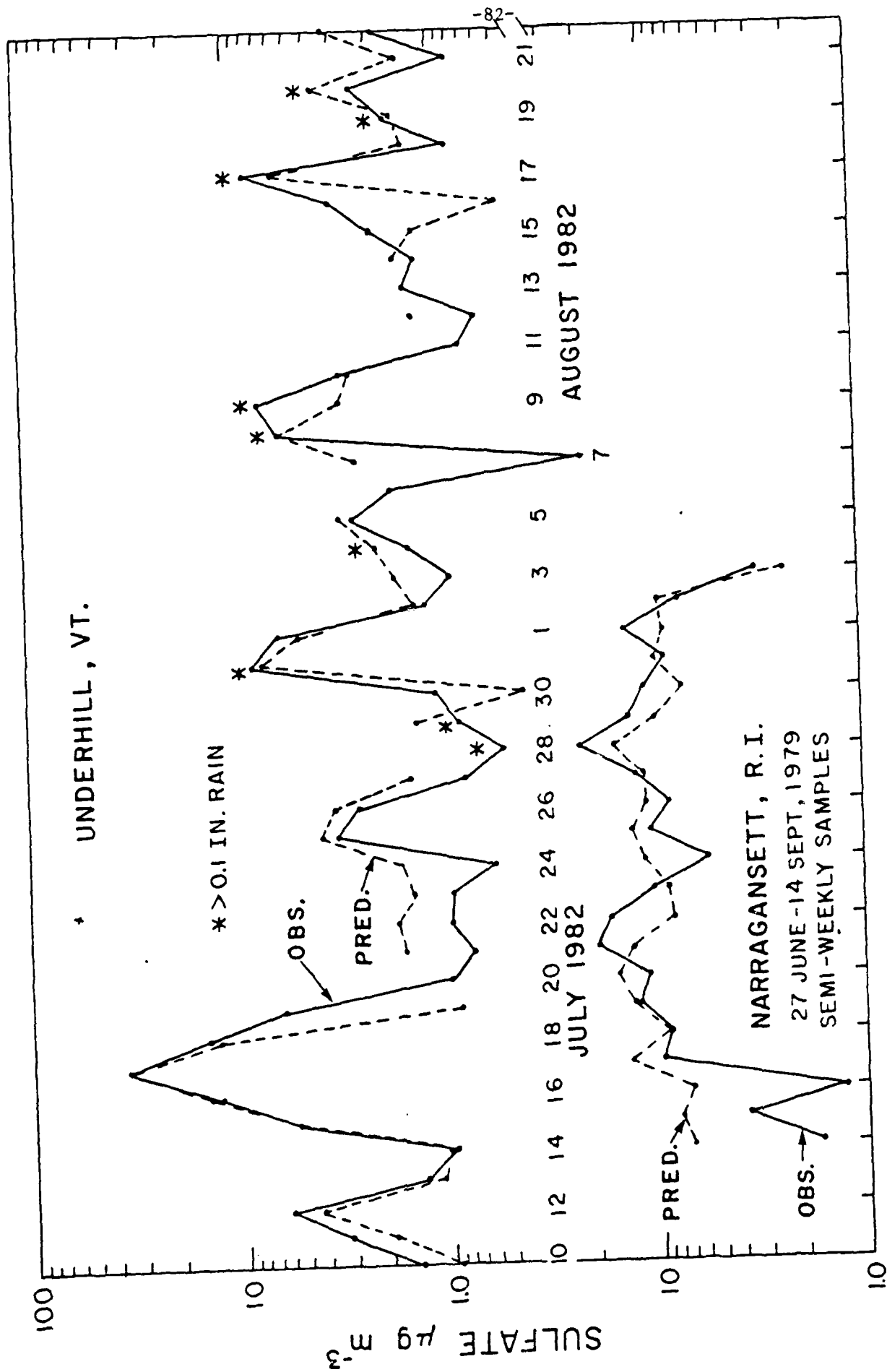
Figure 2.   Observed sulfate at Underhill, Vermont and Narragansett, Rhode Island compared to that predicted from least-squares regression of regional signatures.

Table 1. Elemental signatures for source aerosols in
North America and Europe.

Source	N	As/Se	Sb/Se	xV/Se	Zn/Se	xMn/Se	In/Se(x1000)
Individual sources							
SCANS	5	2.8+0.7	1.14+0.82	24+5	46+19	6.1+4.1	10.4+4.2
WEURS	5	1.92+0.43	1.05+0.29	5.9+1.3	37+4	6.6+1.4	14.3+7.1
WEURH	5	3.5+0.4	0.78+0.27	8.3+4.4	60+26	7.7+4.4	14.5+12.5
EEURF	5	7.3+1.0	1.37+0.31	8.0+1.7	54+3	10.2+2.0	13.4+3.2
EEURS	3	7.3+1.0	1.74+0.10	4.9+1.1	66+4	13.8+2.6	15.2+2.1
EEURH	4	8.9+0.3	1.18+0.12	5.3+1.2	48+5	10.2+6.2	10.2+3.4
NE	4	0.136+0.047	0.46+0.13	11.6+2.6	32+5	9.4+2.4	11.0+5.4
BOS	3	0.71+0.29	0.91+0.46	35+6	37+3	4.2+0.8	5.3+0.5
NYC	3	1.11+0.13	1.78+0.92	11.3+3.0	40+4	6.7+1.8	10.2+4.0
WASH	4	1.48+0.31	0.83+0.12	10.0+1.8	23+5	4.6+2.9	7.2+1.5
MWC	4	0.93+0.14	0.29+0.12	2.0+0.7	11.1+2.9	2.7+1.1	4.3+2.0
SONT	3	8.1+1.2	0.76+0.11	2.0+1.3	57+4	14.0+1.7	51+25
Regional means							
SCANS	5	2.8+0.7	1.14+0.82	24+5	46+19	6.1+4.1	10.4+4.2
WEUR	10	2.7+0.9	0.91+0.30	7.1+3.3	48+21	7.1+3.1	14.4+9.6
EEUR	12	7.8+1.1	1.40+0.30	6.3+2.0	55+8	11.1+4.0	12.8+3.4
ECOAST	14	0.85+0.58	0.95+0.64	16.1+10.7	32+8	6.4+3.0	8.5+3.9
MWC	4	0.93+0.14	0.29+0.12	2.0+0.7	11.1+2.9	2.7+1.1	4.3+2.0
SONT	3	8.1+1.2	0.76+0.11	2.0+1.3	57+4	14.0+1.7	51+25
Continental means							
EUR	27	5.0+2.7	1.17+0.47	9.9+7.6	51+16	8.7+4.2	12.9+6.4
NAMER	21	1.90+2.7	0.80+0.58	11.4+11.0	32+15	6.8+4.2	13.8+17.8

Table 2. An episode of east European aerosol at Sweden and Finland.

Dates of sample	Sulfate ($\mu g\ m^{-3}$)	As/Se	Sb/Se	xV/Se	Zn/Se	xMn/Se	In/Se ($\times 10^3$)
			Rörvik, Sweden				
11-13 January 1982	2.4	3.0	0.67	15.4	69	13.1	17.4
13-15 January 1982	5.4	9.6	2.45	50	52	26.5	31
15-18 January 1982	12.9	4.0	0.8	5.2	49	6.0	<3
18-20 January 1982*	11.1	7.4	1.85	6.0	70	13.0	16.1
20-21 January 1982*	19.5	8.2	1.68	3.8	65	11.7	12.8
21-22 January 1982*	35.5	6.3	1.68	4.8	63	16.8	16.7
22-25 January 1982	8.26	3.3	1.83	4.2	33	4.5	7.6
25-27 January 1982	3.6	1.8	0.98	14.6	31	3.5	13.1
			Ähtäri, Finland				
17-18 January 1982	6.5	3.4	0.60	9.4	54	3.8	7.2
18-19 January 1982	5.3	2.6	0.64	8.0	66	5.7	11
19-20 January 1982*	3.7	5.5	1.3	8.9	58	9.5	15
20-21 January 1982*	19.4	6.6	1.6	5.7	52	13	13
21-22 January 1982*	9.0	6.8	1.5	7.0	56	11	11
22-23 January 1982*	17.8	5.9	1.6	8.3	52	10	10
23-24 January 1982	0.95	4.6	0.86	10	52	7.6	18

*East European aerosol present

Table 3. Two estimates of the relative discriminatory power of various elemental ratios on the 48 signature samples of Table 1.

Elemental ratio omitted	Number of samples misclassified (out of 48)		
	With 12 individual signatures	With 6 regional signatures	With 2 continental signatures
--	1	2	7
As/Se	6	13	13
Sb/Se	1	2	6
xV/Se	3	6	7
Zn/Se	2	3	9
xMn/Se	1	4	7
In/Se	2	2	7
As/Se, xV/Se	13	19	10
xMn/Se, In/Se[*]	2	--	--
Sb/Se, Zn/Se[*]	--	5	--
Sb/Se, Zn/Se, xMn/Se, In/Se[*]	--	--	8

[*]Ratios indicated by stepwise discriminant analysis to be lacking in discriminatory power.

Table 4. Classification of nonsignature aerosol samples
in North America and Europe.

Site	Classified as					
	N. America	Europe	N. America	Europe	N. America	Europe
	(Using 12 individual signatures)		(Using 6 regional signatures)		(Using 2 continental signatures)	
Narragansett, RI	98	3	92	9	94	7
Underhill, Vermont	25	10	22	13	29	6
Rörvik, Sweden	21	45	19	47	28	38
Kecskemét, Hungary	0	22	0	22	0	22
			(Using 5 regional signatures)			
Bear Island (Without In/Se)			1	31		
Barrow, Alaska (Without In/Se)			5	28		
	SONT	NE	BOS	NYC	WASH	MWC
Narragansett, RI	0	17	17	8	37	22
Underhill, Vermont	1	14	1	7	3	9

Table 5. Elemental concentrations (μg m^{-3}) in five source-area aerosols.

	NENG	BOS	NYC	WASH	MWC
As	0.060+0.033	0.49+0.15	2.0+0.2	3.2+0.9	1.54+0.40
Sb	0.143+0.048	0.83+0.41	3.1+0.6	2.1+0.7	0.55+0.20
Se	0.37+0.20	1. 0.60	1.88+0.42	2.4+0.7	1.78+0.79
xV	4.0+1.7	35+6	20+4	23+8	3.4+1.0
Zn	11.1+4.3	37+3	70+17	60+12	18.2+8.0
xMn	2.2+0.3	4.2+0.8	13.0+1.1	9.2+3.4	4.3+2.4
In	0.0028+0.0001	0.0050+0.0040	0.0160+0.0032	0.020+0.006	0.0064+0.0006

Table 6. Contributions of various source regions to elements in

Narragansett aerosol sample GSO 1/6, 7-8 August 1979 (ng m^{-3}).

	WT.	NENG	BOS	NYC	WASH	MMC	TOT.PRED.	OBS.
As	300	0.03	0.06	--	0.20	0.36	0.65	0.67
Sb	30	0.08	0.10	--	0.13	0.13	0.44	0.55
Se	100	0.20	0.13	--	0.15	0.42	0.90	0.90
xV	20	2.20	4.42	--	1.44	0.80	8.9	9.0
Zn	4	6.11	4.08	--	3.76	4.31	18.9	18.4
xMn	0.4	1.21	0.53	--	0.58	1.02	3.34	2.00
In	100	0.0015	0.0006	--	0.00	0.0015	0.0036	0.0040
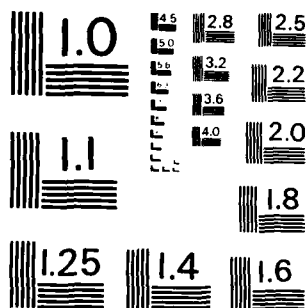
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Table 7. Least-squares regional coefficients for 14 Narragansett
aerosol samples from summer 1979.

Sample	Dates(1979)	$SO_4^=(\mu g\ m^{-3})$	Regression coefficients						Σ(wgtd. fr. resid.)
			NENG	BOS	NYC	WASH	MWC	
GSO 171	13-17 July	8.63	0.66	0.11	0.11	0.02	0.07	0.16
GSO 172	17-24 July	12.32	0.37	0.26	0.12	0.01	0.20	0.18
GSO 173	24-27 July	11.24	0.00	0.36	0.00	0.00	0.56	1.20
GSO 174	27-31 July	19.12	0.00	0.19	0.16	0.00	0.47	1.64
GSO 175	31 July-3 Aug.	16.49	0.76	0.00	0.04	0.00	0.34	2.16
GSO 176	3-8 Aug.	10.28	0.55	0.13	0.00	0.06	0.24	0.09
GSO 177	8-10 Aug.	5.47	0.56	0.08	0.22	0.00	0.23	0.80
GSO 178	10-14 Aug.	10.49	0.30	0.37	0.00	0.00	0.19	1.78
GSO 179	14-17 Aug.	8.31	1.17	0.07	0.19	0.00	0.00	21.15
GSO 180	17-21 Aug.	12.14	0.47	0.35	0.00	0.02	0.00	3.22
GSO 181	21-24 Aug.	22.48	0.38	0.47	0.09	0.00	0.00	0.47
GSO 182	24-28 Aug.	12.90	0.78	0.17	0.00	0.00	0.16	4.77
GSO 183	28-31 Aug.	11.00	0.80	0.05	0.02	0.00	0.14	0.72
GSO 184	31 Aug.-3 Sept.	8.71	0.55	0.16	0.00	0.00	0.27	0.90

E.6.

On the Aerosol Particle Size Distribution Spectrum in Alaskan Air Mass Systems: Arctic Haze and Non-Haze Episodes

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ABSTRACT

Aerosols in central Alaskan winter air mass systems were classified according to size by diffusive separation and light-scattering spectrometry. Particles entering central Alaska from the Pacific Marine environment had number concentrations ranging from 300 to 2000 cm^{-3} (geometric mean 685 cm^{-3}) and unimoda' size spectra, with maximum in number concentration near 1×10^{-6} cm radius.

Air masses entering Alaska from the Eurasian Arctic possessed a factor of two smaller aerosol number concentrations than Pacific Marine systems (*e.g.*, 150–700 cm^{-3}; geometric mean 386 cm^{-3}) but contained a factor of two greater particle volume loading within the fine particle radius range $\sim 5 \times 10^{-7} < r < 1 \times 10^{-5}$ cm. The particles in Eurasian Arctic air masses were bimodally distributed, with maxima in the particle size spectra near $r = 3 \times 10^{-7}$ and 5×10^{-6} cm. Sulfur was the predominant element in all cases studied.

A particle depleted region was present in the size spectra obtained for Eurasian Arctic air masses. The deficiency of particles in the 10^{-6} cm radius range is interpreted as being the result of thermal coagulation taking place between sulfur-rich nuclei (produced at a rate of 10^{-20} to 10^{-18} g cm^{-3} s^{-1} and in sizes $r < 10^{-6}$ cm) and "large" ($r \sim 10^{-5}$ cm) imported primary particles. The primary particles are in the removal-resistant Greenfield Gap ($r \sim 10^{-5}$ cm) and seem to originate in the central Eurasian region.

1. Introduction

This paper describes the size spectrum signature of aerosols in the lower troposphere in central Alaska during Arctic haze and non-Arctic haze episodes. The emphasis is on particles in the radius range 10^{-7} to 10^{-5} cm, though some limited information is also being reported on the size spectrum of particles with radius $r > 10^{-5}$ cm. We were concerned with air masses free of local contamination, "local" referring to distance scales of the order 500 km. Size spectra were measured with a diffusion battery and laser spectrometer in late winter and early spring.

The clean air mass systems studied may be characterized as follows:

1) The winter-Alaskan air masses were minimally affected by local crustal and organic material from vegetation due to the extensive snow-cover.
2) Solar ultraviolet radiation was negligible except for a few periods in March.
3) The air mass systems investigated originated from two surrounding physical environments: Eurasian Arctic and Pacific Marine (Northern Pacific Ocean).

The atmospheric particles, as far as can be determined, were transport. into central Alaska from outside Alaska's bounc ies and probably consist of a combination of primary and secondary particles.

2. Remarks concerning the measurement location

The aerosol size distribution experiments were conducted from Ester Dome Observatory (64°53'N, 148°03'W, 715 m MSL) near the center of the broad valleys draining the Yukon River and its tributaries. Interior Alaska (Fig. 1) is generally the region north and west of the Alaska Range and south of the Brooks Range. It is large enough to permit the identification and tracking of fronts yet small enough to display uniform synoptic weather conditions and climatic uniformity (Bilello, 1974). It has a continental climate because the Alaska Range barrier shields it from strong cyclonic systems in the Gulf of Alaska. The surface is snow-covered and below 0°C from October to April.

In this vast area, the only significant anthropogenic source of pollution is Fairbanks (population 50 000), but the emissions from the city remain under strong and persistent temperature inversions (Benson, 1970) and flow katabatically down the broad flood plains of the Tanana River. At no time during the experiments were contaminant aerosols from the city detectable at Ester Dome Observatory. Aerosol concentration remained constant to within a factor of two over an interval of hours and sometimes days, changing significantly only when meteorological conditions changed on the mesoscale.

On cloud-free days in winter the horizontal visi-
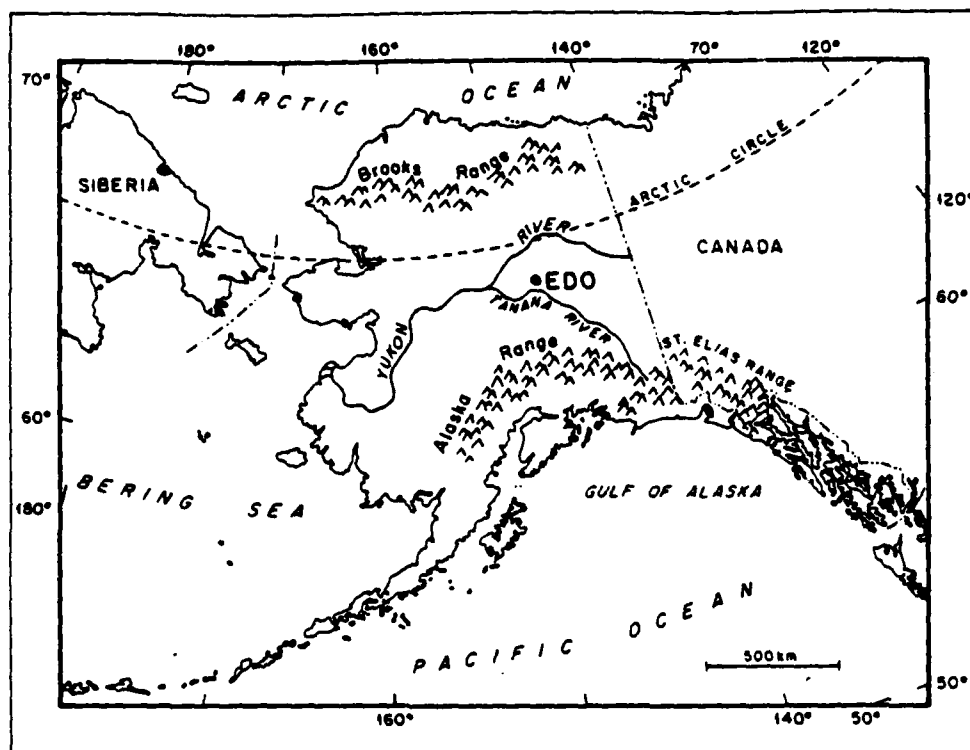
FIG. 1. The geographic region of interior Alaska is north and west of the Alaska Range and south of the Brooks Range. In winter, pollutants from Fairbanks are trapped by strong, persistent temperature inversions and flow down the flood plains of the Tanana River, thereby not affecting Ester Dome Observatory.

bility sometimes lowered from one or two hundred kilometers to several tens of kilometers. These periods of haziness occurred in association with air masses entering Alaska from the Eurasian Arctic. They are examples of the so-called "Arctic Haze" phenomena (Mitchell, 1956; Rahn, 1981a).

3. Experimental method

The size spectrum of the aerosols was determined in the Aitken radius range ($\sim 2 \times 10^{-7} < r < 10^{-5}$ cm) with a diffusion battery using Nuclepore® polycarbonate substrate diffusion screens (Twomey, 1976) with monodisperse pores ranging in diameter from 0.6 to 8 μm. This system was connected by short lengths of stainless steel tubing to keep interstage diffusion losses of particles to a minimum. Since in central Alaska the aerosol concentration often remained constant to within several percent for times of 15 min or longer, one could carry out an entire measurement sequence (which consisted of 16 combinations of diffusion screen pore diameters and air flow rates) by sampling in the free atmosphere. This procedure eliminated systematic errors introduced by the more

usual procedure of holding the air sample in a container. In the latter case, highly mobile small particles are lost by diffusing to the walls of the holding chamber.

Particles transmitted through the diffusion barrier were counted with a photoelectric condensation nuclei counter. The counter was similar in dimensions and expansion ratio to a Nolan–Pollak counter. It employed a light emitting diode sending a paraxial beam of light 0.8 cm diameter along the axis of a humidified stainless steel cylinder, 4 cm in diameter and 75 cm in length. This instrument was calibrated to an estimated relative accuracy of 2% against a convergent beam Nolan–Pollak counter (serial number 16) at the NOAA Station at Barrow, Alaska, which in turn had undergone recent primary calibration.

We have attempted to evaluate the magnitude of errors, especially systematic errors, that could influence the sizes determined from the diffusion battery. Porosity of the filters (the ratio of pore area to filter substrate area) and the distribution of pore sizes in the Nuclepore filters were evaluated by electron microscopy to an estimated accuracy of 5%. Flow rate was measured to 2% accuracy.

The lower radius limit below which particles are not nucleated into droplets in the fog chamber cannot, nfortunately, be specified very accurately. It is likely to be larger than that deduced from the Kelvin equation ($r = 10^{-7}$ cm for the counter used) and may be as large as 5×10^{-7} to 1×10^{-6} cm (Liu and Kim, 1977; Liu and Pui, 1979; Podzimek and Yue, 1982; Sinclair, 1982). Twomey (1976) discusses the uncertainty associated with particle counting using a Nolan–Pollack counter.

The fidelity to which the mathematical inversion program reproduced a size spectrum in the presence of measurement errors was investigated by performing test inversions on simulated data degraded with noise. We employed the nonlinear inversion method described by Twomey (1975). These tests showed conclusively that the mathematical inversion was capable of delineating the major features of an aerosol size distribution spectrum over the radius range $\sim 5 \times 10^{-7} < r < 10^{-5}$ cm. The presence of two modes in the particle size distribution function, separated by a minimum of $\Delta \log r \approx 0.5$, could be unambiguously detected, though three or more modes within the particle range $5 \times 10^{-7} < r < 10^{-5}$ cm were sometimes not recovered with acceptable fidelity. The number concentration and mean modal radii for two modes, in the presence of 15% rms measurement noise, reproduced to ±20 and ±50% accuracy, respectively. Further information on the capabilities and limitatic :s of the nonlinear inversion as applied to diffusion battery measurements is discussed by Gras (1981).

Later in this paper we will discuss certain differences which exist in the size spectrum between haze and non-haze episodes occurring in interior Alaska. The differences that occurred according to numerical calculations conducted on noise-degraded data are quite discernible with the nonlinear inversion and cannot be attributed to systematic error, even for "worse cases" of measurement uncertainty.

The data discussed in this paper were obtained during periods when meteorological conditions allowed aerosol concentrations to remain constant for one hour. Furthermore, the requirement was stipulated that three or more independent measurements made with the diffusion battery repeat within at least ±5% accuracy.

In some cases the aerosol size spectrum was extended to a larger particle radius range (namely $1 \times 10^{-5} < r < 3 \times 10^{-4}$ cm) by using a commercial laser aerosol spectrometer (Particle Measuring System Model LAS-X) which was frequently calibrated with monodisperse latex spheres in the manner specified by the manufacturer. Unfortunately, the laser particle spectrometer was inoperative during much of the time during which the e. ,eriments were being performed, so only six size spectra have th · extended range size distribution information. Acc ,ptable re-

sults were obtained for the differential number concentration in the particle radius range where the two instruments (the aerosol spectrometer and the diffusion battery) overlapped; typic. 'y the agreement between the two was better than a factor of two.

4. Results

Size spectra for particles in air masses which had invaded interior Alaska in the late winter–early spring months, 1982, are illustrated in Fig. 2 and associated aerosol and meteorological parameters are listed in Table 1. The geographical regions reached when tracing backwards from Ester Dome along isobaric trajectories (850 mb) for a period of five days prior to the individual aerosol determinations are listed in column 3.

Any special conditions noted at the station during the time of measurement are noted in column 5 of Table 1; several of the measurements were made when there was visual pervasive haze, definite haze streaks against the sky and/or lowered visibility of the foothills and mountains of the Alaska Range. Sometimes there were cases when visual haze was suspected but difficult to confirm because of localized clouds near the distant mountain ranges or poor illumination. For example, it seemed generally hazy around 13, 14 February (the time of the first two observations listed in Table 1), but we could not be sure that haze was definitely present at the ti ne of measurement. On 4 March, the aureole of scat :red light around the sun was smaller ($\sim 5-10°$ diameter), whiter and brighter than it usually is, possibly arising from residual giant sea salt particles that had been carried in from the North Pacific.

In Table 1, column 6 indicates the number concentration of aerosols n_0, and column 7 lists the accumulated specific volume of aerosol in the fine particle modes (aerosol smaller than 1×10^{-5} cm radius). Thus, on 13 February 1982 the particle concentration ($r > 5 \times 10^{-7}$ cm) was 170 cm^{-3}, and the specific volume occupied by fine-mode aerosols was 0.49 $\times 10^{-12}$ cm^3 per cubic centimeter of air. Assuming the particles are composed of a material of mass density 2 g cm^{-3}, the just-mentioned specific volume would imply a mass loading of 1 μg m^{-3} of particles in the fine mode ($r < 1 \times 10^{-5}$ m). Total particle mass concentrations for aerosols during Arctic haze episodes have been previously estimated to be 5–10 μg m^{-3} (Barrie et al., 1981; Rahn, 1981b).

On the basis of the back trajectory information (column 3 of Table 1) we have placed each size spectrum into one of two categories, "Eurasian Arctic" or "Pacific Marine" (Table 1, last column). On 24 February the back trajectory extended from Ester Dome northwestward to $\sim 80°$N latitude, but then arched over and went southward into the ice-free re-
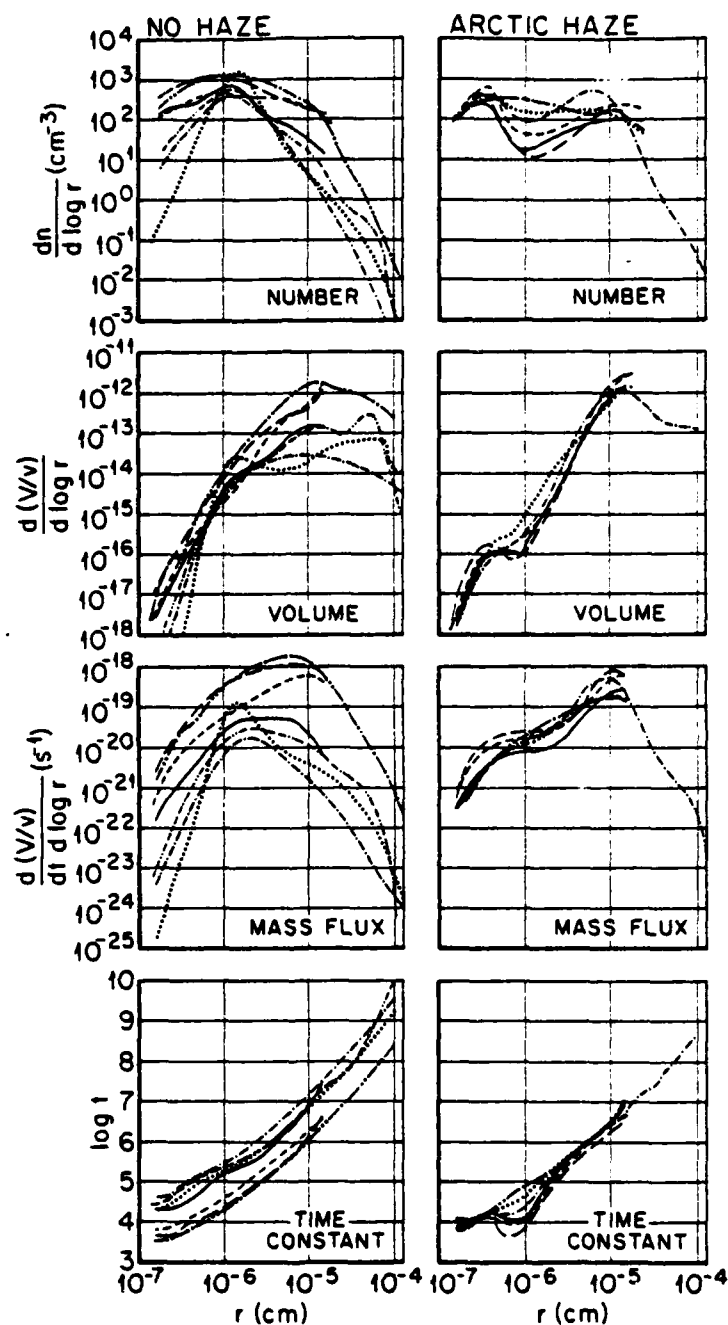
FIG. 2. Top to bottom: (a) size distribution, (b) volume distribution, (c) rate of volume passing through aerosol size spectra (equal to mass flow for a particle density of 1 g cm⁻³) due to thermal coagulation, and (d) coagulation time constant for particles in "no haze" Pacific Marine air mass systems and air mass systems originating from the Eurasian Arctic. Parameters for $r > 1 \times 10^{-5}$ cm were determined by optical techniques, those for $r < 1 \times 10^{-5}$ cm were derived by inversion of diffusion battery measurements.

TABLE 1. Aerosol and meteorological parameters for data graphed in Fig. 2.

Date (1982)	Time (LST)	Trajectory location 5-days back	Tempera- ture (°C)	Special conditions near station	n_0 (cm^{-3})	Final mode volume (10^{-12} cm^3 cm^{-3})	Volume classifi- cation[*]
February 13	1230	North Central Siberia	−18	Haze (?)	170	0.49	EA
February 14	1250	North Central Siberia	−30	Haze (?)	390	0.75	EA
February 21	1530	Central USSR	−30	Visual haze and streaks	400	0.37	EA
February 24	1620	South Bering Sea (flow into high Arctic, then down)	−19	Strong haze	320	0.69	EA (?)
February 27	2130	East Siberia and Bering Sea	−18		560	0.09	PM
March 4	0930	North Pacific	−18	Small, bright solar aureole	770	0.59	PM
March 14	1210	Convergent flow North Pacific and North Siberia	−17		550	0.89	Transitional
March 16	1200	North Pacific	−7	Frontal passage	700	0.07	PM
March 19	1420	North Pacific Sea of Okhotsk	+5		1750	0.72	PM
March 21	1230	Sea of Okhotsk	+10	Snow falling	280	0.04	PM
March 26	1720	Central Siberia- Taymyr Peninsula	−15	Strong haze	710	0.35	EA
April 3	1800	North Pacific	−7		1200	1.6	PM
April 6	1500	North Pacific	+2		400	0.18	PM

* EA, Eurasian Arctic air masses   Geometric Mean   386   0.55
PM, Pacific Marine air masses   Geometric Mean   685   0.23

gion of the Bering Sea, it is thus difficult to know how to classify this trajectory; we have tentatively placed it in the Eurasian Arctic classification. Similarly, it is difficult to know how to classify the air mass characteristic for 14 March since there was convergent flow entering central Alaska from the North Pacific and from the northern Siberian Arctic. We have plotted the size spectra in Fig. 2 separately in accordance with the classification just mentioned. The two "ambiguous" cases were plotted in the Eurasian Arctic classification (24 February is the curve with long dashes; 14 March is the curve extending into the radius range $r > 2 \times 10^{-5}$ cm). These two spectra are intermediate or transitional between no haze (Pacific Marine air masses) and Arctic haze (Eurasian Arctic air masses).

The size spectra for air masses emanating from the Eurasian Arctic (labeled Arctic haze in Fig. 2) are bimodal, with maxima in $dn/d \log r$ near $r \approx 3 \times 10^{-7}$ cm and $r = 8 \times 10^{-6}$ cm, whereas the size spectra for Pacific Marine "no-haze" conditions are monomodal, peaking near 10^{-6} cm radius. The bi-

modal and monomodal nature of Eurasian Arctic and Pacific Marine aerosols seems to represent a fundamental property.

The total particle number concentration shown in Table 1 ($r > 5 \times 10^{-7}$ cm) is larger (geometric mean 685 cm^{-3}) in the set of Pacific Marine spectra than it is for the set of Eurasian Arctic data (geometric mean 386 cm^{-3}). On the other hand, total volume loading in the fine particle radius interval $r < 1 \times 10^{-5}$ cm is greater for Eurasian Arctic air masses (geometric mean 0.55×10^{-12} cm^3 cm^{-3}) than it is for Pacific Marine conditions (geometric mean 0.23×10^{-12} cm^3 cm^{-3}). Arctic haze episodes (Eurasian Arctic air masses) tend to have low total particle number concentrations but high aerosol mass in the radius range $r < 1 \times 10^{-5}$ cm.

Fig. 2c shows the rate of transport of aerosol volume (equal to aerosol mass for a particle density of 1 g cm^{-3}) passing through the aerosol size distribution by coagulation of particles with each other under the action of thermal Brownian motion. It was calculated by using the expression

$$F(x) = \int_0^x n(v) \int_{x-v}^v (u+v)K(v,u)n(u)du\,dv$$

$$+ \int_x^\infty n(v) \int_0^x uK(v,u)n(u)du\,dv, \quad (1)$$

where $F(x)$ is given in $cm^3\ s^{-1}\ cm^{-3}$ of air, and $K(u, v)$ is the product of collision probability and collision efficiency for particles with volumes u and v present in number concentrations $n(u)du$ and $n(v)dv$ interacting with each other under thermal movements. The calculations of Fig. 2c employed coagulation coefficients computed according to Walter (1973). Eq. (1) was solved numerically with quadrature using increments of $\Delta\ \log r = 0.01$.

Coagulative mass flux passing through the size distribution (shown in Fig. 2c) would be constant between r_1 and r_2 for the steady state conditions of particles of radii $r = r_1$, being continually created by homogeneous nucleation of trace gases, growing by coalescence to larger sizes and finally being removed by external processes at $r = r_2$.

It would seem from Fig. 2c that quasi steady-state coagulative mass transfer processes are taking place approximately over the radius interval $10^{-6} < r < 10^{-5}$ cm for Pacific Marine "no haze" conditions. On the other hand, in Eurasian Arctic air masses, the coagulative flux peaks distinctly at $r \approx 10^{-5}$ cm. One might infer from this behavior that the clean "no haze" Pacific Marine air masses are in or approaching a coagulative quasi steady-state condition (where small particles nucleate, pass by thermal coagulation to larger sizes and then are removed), whereas this process is beginning to break down for aerosols in contaminated air masses originating in the Eurasian Arctic. A possible reason for this behavior, as explained later, is the coexistence of primary pollution particles of $r \sim 10^{-5}$ cm, which efficiently remove small nuclei by coagulating with them.

Fig. 2d shows the time constant over which significant changes in the aerosol size spectrum (over one decade of particle size) would occur due to particle coagulation under Brownian motion. Though there are a variety of time constants one can use to describe coagulative processes, the one graphed is

$$t_c = \left[\frac{4\pi r^3}{3F(r)}\right]\left[\frac{dn(r)}{d\ \log r}\right]. \quad (2)$$

The time constant t_c provides an idea of the length of time over which significant changes can take place within $\pm$ one-half decade of particle size in the observed aerosol size spectrum by thermal coagulation in the hypothetical case of an abrupt change or cutoff in the feed particles entering by gas-to-particle conversion. Smaller particles have the highest mobilities, hence the shortest time constant. Features of the

particle size distribution in Fig. 2 for particles smaller than $r \sim 2 \times 10^{-6}$ cm would change noticeably by coagulation in times less than the time of air mass transport, which was always greater than one day. However, particles larger than $r \approx 2 \times 10^{-6}$ cm would take longer to change significantly and the presence of considerable numbers of particles present at or near $r = 10^{-5}$ cm would take ~ 100 days to re-establish themselves, once removed by coagulation. From this it may be inferred that the large mode in Eurasian Arctic air masses has not been produced by coagulation.

5. Discussion

In all instances, particles were present in small enough size (i.e., $r < 1 \times 10^{-6}$ cm) and large enough concentrations to alter significantly by thermal coagulation in times of several hours (Fig. 2d), which indicates that particles of $r < 10^{-6}$ cm are being supplied to the atmosphere by nucleation under low sunlight illumination conditions typical of the winter sub-Arctic environment. The growth of the nucleated embryos for no haze Pacific Marine air flow is surmised to proceed by thermal coagulation, as evidenced by the relative constancy of coagulative mass flux in the radius interval 10^{-6} to 10^{-5} cm. According to Fig. 2c, gas-to-particle conversion must be taking place at a rate of 10^{-20} to $10^{-18}\ g\ cm^{-3}\ s^{-1}$ (assuming a particle mass density of 1 $g\ cm^{-3}$).

It was not feasible to determine the composition of particles smaller than $r \approx 1 \times 10^{-5}$ cm, but $\sim 98\%$ of particles near this size limit contained sulfate, as evidenced by the formation of reaction rings upon impaction on a $BaCl_2$ substrate (Ayers, 1977; Bigg et al., 1974) and by the existence of strong sulfur X-ray lines in X-ray spectrograms of the particles. No attempt was made to differentiate different compounds of sulfate, but probably the fine Aitken particles consist of sulfuric acid droplets and ammonium sulfate (Bigg, 1980). Aerosols from the Gulf of Alaska seem to be representative of a more general tropospheric background sulfate aerosol (Haaf and Jaenicke, 1980). Similar aerosols, by chemistry, have been detected in the stratosphere (Bigg, 1976) and over the Antarctic ice sheet (Bigg, 1980).

The source and composition of the background gas nucleating the sulfate aerosols is unknown, but it may consist of Marine biogenically-produced long-lived dimethyl sulphide or carbon bisulphide (Logan et al., 1979; Sze and Ko, 1979). It is not clear to what extent anthropogenic pollution is a contributor to the tropospheric background sulfate aerosol.

The background Pacific Marine aerosol concentration observed in interior Alaska has a geometric mean number concentration two to three times larger than that observed at Barrow, Alaska during non-Arctic

haze conditions (Bodhaine, et al., 1981), whereas the number concentration of aerosols in Eurasian Arctic air masses are comparable for interior Alaska and Point Barrow. The Pacific Marine air masses affecting interior Alaska have a travel time of one to several days, whereas the clean non-Arctic haze air masses observed at Point Barrow must be less marine in nature.

The bimodality of Arctic haze aerosols may be interpreted on the basis of a coagulation model described by Walter (1973). Walter's calculations indicate that under the assumption of a constant rate of production of embryonic nuclei,[1] a quasi-stationary, monotonically decreasing, aerosol-size distribution function sets up under the action of thermal coagulation and within a time of ~1 day. If large (i.e., $r \sim 2 \times 10^{-5}$ cm) particles are now superimposed on this system, Walter showed that their presence introduces a depletion region or gap in the particle size distribution function due to the very nonlinear processes of interparticle thermal coagulation. For example, when the nuclei production rate is 100 cm^{-3} ($r = 1.2 \times 10^{-7}$ cm) and when the large ($r > 1 \times 10^{-5}$ cm) particle concentration is maintained at ~550 cm^{-3}, the gap or depleted region in the size spectrum extends from $r = 4 \times 10^{-7}$ to $r = 2 \times 10^{-6}$ cm, approximately corresponding to that observed in the Eurasian Arctic size spectra.

The bimodality of the Arctic haze aerosols is therefore simply explained by hypothesizing that there exist enhanced (over the quasi-stationary state) numbers of $r \approx 1 \times 10^{-5}$ cm particles present in Eurasian Arctic air masses and that these large primary particles are superimposed on the more general background secondary aerosol, which is being fed mass at a rate of 10^{-18} to 10^{-20} g cm^{-3} s^{-1}. Since Arctic haze is suspected to derive from pollution sources (Rahn, 1981), the gap in the Aitken particle size distribution for Eurasian Arctic air masses represents, according to this hypothesis, a manifestation of primary pollution aerosol traveling to Alaska from distances of several thousand kilometers. Coal fired power plants and other industrial activity employing combustion, inject large amounts of $r \sim 2 \times 10^{-5}$ cm particles directly into the atmosphere (McElroy, et al., 1982). Particles of radius ~ 10^{-5} cm are removal-resistant, being too large to be efficiently removed by diffusive processes and too small to be removed very efficiently by inertially controlled processes (within the Greenfield Gap). Therefore, they can be carried for long distances. In the concentrations found (~10 cm^{-3}) they coagulate slowly with characteristic time constants of 10–100 days.

' It was assumed by Walter that embr...s are formed at a constant rate and within a narrow size int val centered at $r = 1.0 \times 10^{-7}$ cm.

The presence of a mode of large (i.e., $r \approx 10^{-5}$ cm) possibly pollution-derived aerosol entering Alaska modifies the general background tropospheric aerosol upon which it is superim, sed considerably because of coagulative interactions between the "pollution" and "natural" aerosol. Walter's solution of the coagulation equation and our observation suggest that the most obvious manifestation of the nonlinear coagulative interaction is to deplete the size spectrum in particles of $r \sim 10^{-6}$ cm. This interaction, according to the solutions of the coagulation equation leads to the somewhat ironic conclusion that the introduction of a large, but submicron, pollution aerosol component into an air mass containing a general tropospheric aerosol lowers, rather than raises, the overall aerosol number concentration.

It is unfortunate that no information was acquired in these experiments on the size spectrum of optically-active ($0.1 < r < 0.5$ μm) particles for Eurasian Arctic air mass systems (the LAS-X spectrometer was out of service during the strong haze episodes). The one case plotted in Fig. 2 where size information is available (14 March) was a transitional episode, not being clearly identifiable as Pacific Marine or Eurasian Arctic. In all instances (14 March included), the optical extinction coefficient is calculated to be $\beta < 5 \times 10^{-7}$ cm^{-1} at wavelength 500 nm.

Information of the size distribution of "large" (i.e., $r > 1 \times 10^{-5}$ cm) particles in Arctic haze has been discussed by Heintzenberg (1980); the general features of our size spectra for Arctic haze coincide rather well with his in the radius interval $5 \times 10^{-6} < r < 10^{-4}$ cm. Heintzenberg's inversion technique (inversion of multi-wavelength Nephelometer data and n_0), however, was insensitive to the particle size range $r < 5 \times 10^{-6}$ cm so his data do not show the bimodality of Arctic Haze.

Finally, we note that Haaf and Jaenicke (1980) found that aerosols at a remote mountain location and aerosols measured during the 1978 North Atlantic FS "Meteor" expedition, exhibited monomodal characteristics with maxima in dn/d log$r$ near $r = 10^{-6}$ cm during night; but they found evidence of a smaller mode (estimated to be near $r = 2 \times 10^{-7}$ cm) existing during sunlit conditions. The Pacific Marine aerosol reaching central Alaska seems similar to that reported by Haaf and Jaenicke for dark conditions.

6. Conclusions

We reached the following conclusions about aerosols in Eurasian Arctic and "clear" Pacific Marine air masses:

• Pacific Marine and Eurasian Arctic air mass systems imported to Alaska over transport pathways of 500–4000 km show systematically different aerosol

￿ize distribution spectra. Eurasian Arctic aerosols ave a bimodal distribution with maximum in number concentration near $r = 3 \times 10^{-7}$ and 5×10^{-6} cm whereas Pacific Marine system aerosols have unimodal size spectra with maximum particle concentration at $r \approx 10^{-6}$ cm.

• Eurasian Arctic air masses contained approximately twice the amount of volume (0.55 versus 0.23) in the fine particle mode ($r < 10^{-5}$ cm) than Pacific Marine air mass systems that enter interior Alaska. The mean particle number concentration, however, was twice as low for Eurasian Arctic air mass systems (386 cm^{-3}) than it was for Pacific Marine (685 cm^{-3}) systems. Eurasian Arctic aerosol tends to be characterized by a relatively large volume/number ratio.

• Pacific Marine air mass systems imported into central Alaska in late winter are deficient in "giant" ($r > 1$ μm) and optically-active ($0.1 < r < 0.3$ μm) particles, but relatively rich in fine (apparently sulfur) particles ($r \approx 10^{-6}$ cm), having, in general, coagulative lifetime less than the time of transport. It has been concluded that gas-to-particle nucleation takes place at a rate of 10^{-18} to 10^{-20} g cm^{-3} s^{-1} in the Pacific Marine systems under the absence of ultraviolet radiation.

• There is evidence from the bimodal nature of the size spectra that air masses originating in the Eurasian Arctic ($\sim$4000 km from central Alaska) are enriched in removal-resistant primary particles in the Greenfield Gap ($r \approx 10^{-5}$ cm). The coexistence of a primary (presumably pollution) component and freshly nucleated particles produces a reduction in coagulative mass transfer through the aerosol size spectra in the size range ($1 \times 10^{-6} < r < 5 \times 10^{-6}$) and a maximum in coagulative mass transfer at $r \approx 10^{-5}$ cm.

• Freshly produced nuclei from gas to particle conversion attach relatively rapidly by thermal coagulation to coexisting primary particles, resulting in a relative reduction in particle number concentration. In central Alaska, we find evidence that this phenomenon results in particle concentrations being lower for "polluted" Eurasian Arctic air masses than for "clean" Pacific Marine air masses. We caution against using total particle concentration as a measure of air degradation at remote locations. Aerosol mass loading would seem to represent a less ambiguous measure of anthropogenic influence.

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II.   Renewal Proposal: 1 October 1983 -30 September 1986 (URI)

    A.   Introduction and rationale

        During the last three years, the basic character of our ONR
Arctic studies has changed. Three years ago, we were still working for
Arctic haze to be accepted as a scientific fact and to attract additional
research groups to study it. We had just completed the Second Symposium
on Arctic Air Chemistry, at the University of Rhode Island, which was
attended by 46 people from six countries. In spite of all this effort,
Arctic Air Chemistry was still a very limited field.

        Much is different now. Due mostly (we believe) to the symposium
and the publicity it received by being published in a special issue of
Atmospheric Environment, Arctic air chemistry is suddenly very popular.
Dr. B. Ottar of the Norwegian Institute of Air Research, a long-term
collaborator with the University of Rhode Island, received a five-year
contract from British Petroleum for research in the Norwegian Arctic. The
potential climatic effects of the Arctic aerosol are being evaluated by a
number of different groups. In spring 1983, there were no less than five
research aircraft operating in the Norwegian and Alaskan Arctic! (We
feared for a collision.) Of NOAA/GMCC's four Baseline Monitoring
Observatories, Barrow is currently the most newsworthy, having surpassed
the long-time leader Mauna Loa.

        In short, we have accomplished our goal of establishing Arctic air
chemistry as a recognized discipline. The time between when we first
realized the importance of pollution aerosol at Barrow and when everyone
else realized it was just about five years.

        As more researchers entered the field, we were able to stop being
generalists and return to being trace-element specialists. This
opportunity came at exactly the right time, because it was during these
last three years that we were first in a position to devise a system of
regional elemental tracers which could determine with confidence and
directness where the sources of Arctic aerosol really were. Recently, we
have devoted ourselves nearly exclusively to this task, and because of
its success so far, wish to continue for the foreseeable future.

        The field of elemental tracers is too big and too important to be
restricted to the Arctic, however. The ability to determine the source
area of a pollution aerosol up to thousands of km from its source is so
valuable in so many areas that we are now diversifying our efforts
considerably. During the past two years, we have become deeply involved
in the acid-precipitation question in the northeastern United States, by
using elemental tracers to determine the source areas of pollution
aerosol there. We are now being funded for this work by EPA, DOE and the
Ohio Electric Utilities Institute (see Section II.D for details), and as
a group are devoting at least half our time to it. Ultimately, we expect
to expend roughly two-thirds of our efforts on non-Arctic applications of
elemental tracers.

        Another important change was the relation between us and the
University of Alaska. As we at URI have come to spend more and more time
on elemental tracers, our interaction with the University of Alaska has

of necessity declined. This situation should not change appreciably in the near future. To recognize this _de_ _facto_ divergence, we have decided that the two groups should deal with ONR individually from now on. Thus, this renewal proposal is for URI only. Because of our additional work in other areas, we have decreased the budget.

B.   **Specific projects**

1.   **Sampling and analysis of Barrow surface aerosol**

We are continuing to collect aerosol samples at the GMCC Baseline Observatory in Barrow even though we no longer analyze them all. The GMCC management is more than willing to work with us under these ground rules, and so we will continue. The ~mples will be used primarily for special studies, as the need arises   Last winter we had two such occasions. The first was associated wit   he still-unexplained plume from Bennett Island in February 1983. Care   analysis of our samples before, during and after the time when th   'ume should have reached Barrow showed nothing unusual, at least a   >a ground. The other special period was during the AGASP flights in Mt ... '83, when daily samples were taken to better coordinate the fligh. .ear Barrow (during the rest of last winter, semi-weekly samples were taken).

Our elemental-tracer system has revealed that the Barrow aerosol takes on only a limited number of different compositions, each of which can be related to distinct point and area sources in Eurasia. One of the major goals of further analysis of the Barrow samples will be to investigate these aerosols during the three winters for which we have daily samples (our detailed analysis of the Barrow aerosol has been based on only semi-weekly samples so far). The first of these winters is already partially analyzed--we will finish it during the next year or so. Major questions to be addressed include:

.   Do the multi-elemental analyses show that a given type of aerosol remains at Barrow for several days at a time, as suggested already by the noncrustal Mn/V ratios from the first winter? (This is very different from the Norwegian Arctic, where air masses and aerosols change more rapidly during much of the winter.)

.   How well can ground-level aerosol at Barrow be related to aerosol aloft in the Eurasian Arctic that we are also measuring?

.   Can these Eurasian samples be used to give an idea of the time it takes air masses to move across the Arctic to Barrow?

.   Are ground-level aerosols at Barrow noticeably more homogenized than they are in the Eurasian Arctic?

.   How often is the Noril'sk signature seen? (Until now, we have seen it in only one of 50 samples.)

.   Are _bona_ _fide_ North American aerosols _ever_ seen at Barrow?

.   Are any signatures seen at Barrow for which we do not know the source?

.   Can the detailed signatures at Barrow be related to large-scale meteorological features in the same way that the Mn/V ratio was (Raatz thesis)? Do any new ideas about transport result?

2.   Particle-size distributions of the Barrow aerosol, (Lewis, M.S. thesis).

This M.S. thesis of Ms. Noëlle F. Lewis of URI will be completed very early in this project. At present, she is scheduled to defend it in September or October 1983. After that, she will prepare two or three articles for publication.

3.   The Arctic Gas- and Aerosol-Sampling Program (AGASP)

As noted in Section I.A.1, four members of this project participated in the AGASP flights of March and April 1983. During the first year of this project, we will be analyzing our samples, comparing results with those of other participants, and preparing them for presentation at the Third Symposium in May 1984. These flights are of considerable interest to us for several reasons: the Alaskan flights came during the heaviest haze of the season, stratospheric aerosol from El Chichon volcano appears to have been intercepted once or twice over Alaska and Greenland, and much of the flying near Norway took place in air masses which had come strongly from the western Soviet Union.

There has already been talk about possible AGASP II and AGASP III experiments. We will participate in all subsequent AGASP's.

4.   Aerosol in the Norwegian Arctic.

Through previous cooperation with Dr. B. Ottar and the Norwegian Institute for Air Research (NILU), we have determined that aerosols at Spitsbergen and Bear Island have elemental signatures which can be identified with Eurasian sources. (See Section I.E.5 for examples of signatures at Bear Island.) During a recent visit to NILU. K. Rahn and B. Ottar agreed to a cooperative program in which URI would analyze NILU's recent aerosol samples taken as part of their BP study. The data will enhance NILU's understanding of their samples, and will greatly aid URI's attempts to broaden its data base in the Arctic. The first group of samples has arrived at URI, and consists of 127 exposed filters from 9 ground sites taken nearly simul·aneously during March 1983. Among the sites are such interesting locations as Spitsbergen, Bear Island, Hopen (just east of Spitsbergen), and Jan Mayen. These samples should be especially valuable to us, for we have never had a chance to examine the Arctic aerosol on such a small scale before. The results should also offer a great deal of information about diffusion vs. organized transport in the Arctic.

5.   Elemental signature of the Nikel' smelter.

In conversations with Dr. B. Ottar and others at NILU, it became apparent that they were quite concerned about the influence of a Ni-Cu smelter at Nikel' on their samples throughout the Norwegian Arctic. This smelter is located in the extreme northwestern USSR, just a few km from the Norwegian border. Because NILU's SO_2 samplers in the

area have recorded extremely high concentrations with winds from the direction of the smelter, NILU has come to feel that Nikel' may be a stronger source than is presently recognized.

It would therefore be of interest to determine the elemental signature of Nikel' and see whether it is indeed detectable in other parts of the Norwegian Arctic. To aid in this, NILU has provided us with four low-volume filter samples taken at border sites approximately 20 km from the smelter, during periods when SO_2 was extremely concentrated (150-700 µg m^{-3}). We have begun to analyze these filters, with great success so far. As, In and Mo are already seen to be highly enriched in the Nikel' plume.

While the smelter at Nikel' is not the only one on the Kola Peninsula, nor necessarily the largest, it is certainly a worthy object of study. Its signature will be compared with those we have developed for other smelters in the Noril'sk complex and the Sudbury Basin.

6.   The URI European Aerosol-Sampling Network

The URI European Aerosol-Sampling Network was begun in 1981 to measure the elemental signatures in various parts of Europe and compare them with signatures in the Arctic. It has been a huge success (Section I.B.). During the next years, we will analyze these samples further, and arrange for additional samples to be taken as needed to supplement our picture. For example, we have a complete year of samples from Finland which we have not been able to analyze yet. We expect to expend considerable effort on the European Aerosol-Sampling Network during the next three years.

7.   Aircraft sampling in the Eurasian Arctic

During the next three years, we will also be devoting a large part of our effort to analyzing aerosol samples from the Eurasian Arctic provided to us by the Air Force. Now that this is an official program between ONR and the Air Force, we expect to receive filters regularly, and will use them to study the vertical distribution of Arctic aerosol, its patterns of injection into the Arctic from Eurasia, and to develop signatures for the Eurasian Arctic and compare them with signatures in the Alaskan and Norwegian Arctic. Seasonal variations will also be studied.

8.   Bromine in the Arctic atmosphere.

Our cooperative effort on bromine in the Arctic atmosphere will also continue. Dr. Walter Berg of the National Center for Atmospheric Research is presently leading this program, and we are pleased to be part of it. He and colleagues are measuring gaseous and particulate bromine during selected intensive field periods at Barrow; we contribute year-round data on particulate bromine from Barrow and our other sites throughout the Arctic, as well as vertical information from our aircraft samples. One major article on this work has already been accepted by Journal of Geophysical Research; a second smaller one is being prepared.

9.   Third Symposium on Arctic Air Chemistry

The Third Symposium on Arctic Air Chemistry will be
held 7-9 May 1984 in Toronto. It will be hosted by Dr. L.A. Barrie of
the Canadian Atmospheric Environment Service and chaired by K. Rahn of
URI. The Canadians are taking care of all the logistical arrangements,
Barrie and Rahn will select the papers jointly for presentation, and K.
Rahn will probably again serve as guest editor for an issue of
Atmospheric Environment in which all the papers will be published. Other
than travel funds for the URI group, nothing will be required of ONR.

C.   Facilities available

Most of the work proposed here will be done in the Rhode
Island Nuclear Science Center (RINSC), where the URI Graduate School of
Oceanography's Center for Atmospheric Chemistry Studies/Arctic Section is
located. The RINSC swimming-pool reactor operates at two megawatts and
delivers a thermal neutron flux of $3 \times 10^{12} n \ cm^{-2} s^{-1}$ at the
irradiation sites. Counting equipment presently available to GSO
investigators at the RINSC includes five large Ge(Li) solid-state
detectors (efficiency 7% to 25% relative to NaI (Tl) crystals) and
associated electronics, which may be used with Nuclear Data Model 2200 or
Canberra Industries Model 8100 4096-channel analyzers or a Digital
Equipment Corporation PHA-11 pulse height analysis system. Gamma spectra
are analyzed on either the main campus IBM 370-65 computer or in the Bay
Campus PRIME system, both via magnetic tape output. For the PHA-11
system, spectra may be analyzed directly on the PDP-11/40 computer which
is part of the system. During the early stages of this project, we
expect to supplement this counting equipment with a new $90,000 system
bought mostly with EPA funds. This new equipment will be the property of
our Arctic group, and should increase our analytical efficiency by at
least a factor of two. In the near future, we hope to further supplement
this equipment with funds from other sources, possibly including ONR.

Also located at the RINSC is complete atomic absorption analysis
laboratory, with three Perkin-Elmer instruments (Models 503, 603 and
5000), HGA-2000 and HGA-2100 heated graphite atomizer attachments, Models
AS-1 and AS-40 sample changers, a HGA-500 programmer, two LFE model
LTA-550 low-temperature ashers, and other accessories. For a standard
user fee, this laboratory is available to all GSO investigators.

Also in the RINSC are two chemical laboratories, a large Class 100
clean laboratory, two smaller clean benches and a small machine shop. A
larger machine shop is located on the main campus.

For analysis of sulfate, one of the chemistry laboratories has a
Varian Series 634 UV-visible spectrophotometer with autosampler and DR37
digital printer. Other facilities available through the Center for
Atmospheric Chemistry Studies and the Graduate School of Oceanography
include an Alden facsimile machine for receiving meteorological maps; a
Dionex ion chromatograph for analysis of sulfate, sulfite, nitrate, etc.;
and two electron microscopes, one with microprobe attachment.

D. Current support and pending applications

Dr. Kenneth A. Rahn - Research Professor, University of Rhode Island

Title	Agency	Duration	Amount	P.I. Time
Current support				
Arctic Haze: Natural or Pollution? (This contract, N00014-76-C-0435; with Dr. G. Shaw of University of Alaska)	ONR	1 Oct 1980- 30 Sept. 1983 (renewal expected)	$177,983 FY83 (URI portion $137,363)	75%
Elemental tracers for local vs. distant source areas of pollution aerosol in the Northeast	OEUI	7/15/82- No end date	$32,029	17%
Boron as a tracer of aerosol from combustion of coal (with Dr. T.R. Fogg of URI)Grant DE-FG22-82-PCS1260.	DOE	9/15/82- 8/31/83	$39,994	8%
Pending applications				
Arctic Haze: Natural or Pollution?(This Contract, N00014-76-C-0435)	ONR	10/1/83- 9/30/86	$144,186 FY84	50%
Elemental tracers applied to transport of aerosol from Midwest to Northeast	EPA	4/1/83- 3/31/84	$149,671	25%
Elemental tracers in northeastern precipitation.	DOE	12/1/83- 5/31/86 (To be submitted late August 1983)	$300,000 (Approx.)	25%

E. **Budgets – FY84, 85, 86**

Fiscal year 1984

(1) Salaries

Principal Investigator Dr. Kenneth A. Rahn Research Professor – 4 months	$12,500	
Mr. Douglas H. Lowenthal Research Specialist – 12 months	23,000	
Graduate student – 12 months Level II	8,500	
Ms. Carla N. Bennett Administrative Assistant – 6 months	6,000	
TOTAL SALARIES		$50,000

(2) Staff benefits

23.6% of nonclassified ($35,500)	8,378	
33.3% of classified ($6,000)	1,998	
TOTAL STAFF BENEFITS		10,376

(3) Permanent equipment

Gamma-counting chain for new neutron-activation analytical system (includes gamma detector, amplifier, analog-to-digital converter, interface, power supply, pulser, lead shield.)	20,000

(4) Expendable equipment and supplies — 5,000

(5) Travel

Domestic:
1 RT Providence-Barrow & 5 days perdiem	$2,000	
Third Symposium on Arctic Air Chemistry, Toronto (4 persons)	3,000	
Miscellaneous meetings	2,000	
Total Domestic Travel		7,000

Foreign:
GAF Meeting, West Germany	1,200	
October 1984 (KAR)		
Total Foreign Travel		1,200
TOTAL TRAVEL		8,200

(6) Publications   1,500

(7) Other

Computer	2,000
Maintenance of sampling and analytical equipment	1,500
Freight	1,000
Telephone	1,000
Meteorological maps	700
Tuition for graduate student	2,500
Illustration services	1,000

TOTAL OTHER   9,700

(8) Indirect charges

47.9% of MTDC ($82,276)   39,410
(excluding capital equipment, graduate student
tuition, academic computer center)

TOTAL COSTS $144,186

Fiscal year 1985

(1) Salaries

Principal Investigator Dr. Kenneth A. Rahn Research Professor - 3 months	$10,000
Mr. Douglas H. Lowenthal Research Specialist - 12 months	24,500
Graduate student - 12 months Level II	9,000
Ms. Carla N. Bennett Administrative Assistant - 6 months	7,000

TOTAL SALARIES $50,500

(2) Staff benefits

23.6% of nonclassified ($34,500)	8,142
33.3% of classified ($7,000)	2,331

TOTAL STAFF BENEFITS 10,473

(3) Permanent equipment

Gamma-counting chain for new neturon-activation 20,000
analytical system (includes gamma detector,
amplifier, analog-to-digital converter, interface,
power supply, pulser, lead shield).

(4) Expendable equipment and supplies 5,000

(5) Travel

Domestic:
1 RT Providence-Barrow & 5 days periem	2,000
Miscellaneous meetings	2,000

Total Domestic Travel 4,000

Foreign:
Visit to agencies in URI European Aerosol-Sampling Network	3,000

Total Foreign Travel 3,000

TOTAL TRAVEL 7,000

(6) Publications 1,500

(7) Other

Computer	2,000	
Maintenance of sampling and analytical equipment	1,500	
Freight	1,000	
Telephone	1,000	
Meteorological maps	700	
Tuition for graduate student	2,800	
Illustration services	<u>1,000</u>	
TOTAL OTHER		10,000

(8) Indirect charges

47.9% of MTDC ($81,673)   39,121
(excludes capital equipment, graduate student
tuition, academic computer center)

TOTAL COSTS   <u>$143,594</u>

Fiscal year 1986

(1) Salaries

Principal Investigator Dr. Kenneth A. Rahn Research Professor - 3 months	$11,000	
Mr. Douglas H. Lowenthal Research Specialist - 12 months	26,000	
Graduate student - 12 months Level II	10,000	
Ms. Carla N. Bennett Administrative Assistant - 6 months	8,000	
TOTAL SALARIES		$55,000

(2) Staff benefits

23.6% of nonclassified ($37,000)	8,732	
33.3% of classified (8,000)	2,664	11,396

(3) Permanent equipment

PRINTRONIX high-speed printer for new neutron-activation system	20,000

(4) Expendable equipment and supplies   5,000

(5) Travel

Domestic:

1 RT Providence-Barrow & 5 days perdiem	2,000
Miscellaneous meetings	2,000
Total Domestic Travel	4,000

Foreign:

GAF 1986 Annual Meeting, West Germany	2,000
Total Foreign Travel	2,000
TOTAL TRAVEL	6,000

(6) Publications   2,000

(7) Other

Computer	3,000
Maintenance of sampling and analytical equipment	1,500
Freight	1,000

(7) Other (cont.)

Telephone	1,000
Meteorological maps	800
Tuition for graduate student	3,000
Illustration services	1,500
TOTAL OTHER	**11,800**

(8) Indirect charges

47.9% of MTDC ($88,196) (excluding capital equipment, graduate tuition, academic computer center)	42,246
TOTAL COSTS	**$153,442**

F. Comments on the budgets

Each of the three annual budgets proposed here is less in real dollars than was the URI portion in the final year of our previous contract period, FY1983. Rapidly rising institutional charges at the University of Rhode Island (fringe benefits and overhead) have forced us to reduce other items correspondingly. The principal cuts have come from the Principal Investigator's salary, which has gone from 9 months support in FY83 to the 4, 3 and 3 months proposed here. These reductions bring his support in line with the actual effort given to this project, as his efforts in other areas (such as acid precipitation) increase.

We are requesting $20,000 for permanent equipment each of the three years. This project has purchased very little equipment over the years; we wish to make up for this now by systematically supplementing our analytical facilities at URI. We have just been awarded $94,000 from EPA for the nucleus of a state-of-the-art neutron-activation system, which will be the heart of our future efforts in atmospheric tracers. To fill it out, we must use other sources, of which ONR will be one. Completing the system will require an additional $200,000.

Our travel budgets are all smaller than in the past. This is allowed by less field work in the Arctic and greater reimbursement of Dr. Rahn's travel from other sources.

<u>NAME</u>:   Kenneth A. Rahn

<u>EDUCATION</u>:   Massachusetts Institute of Technology
B.S. in Chemistry, 1962

University of Michigan
Ph.D. in Meteorology, 1971

<u>PROFESSIONAL
EXPERIENCE</u>:

1983-Present	Research Professor, Graduate School of Oceanography University of Rhode Island
1980-1983	Associate Research Professor, Graduate School of Oceanography, University of Rhode Island
1979 (Summer)	Visiting Scientist, Norwegian Institute for Air Research, Lilleström, Norway
1976 - 1979	Research Associate, Graduate School of Oceanography, University of Rhode Island
1975 - 1976	Invited Visiting Scientist, Max-Planck-Institut für Chemie, Mainz, W. Germany.
1973 - 1975	Research Associate, Graduate School of Oceanography, University of Rhode Island
1971 - 1973	Research Associate, Institute for Nuclear Sciences, University of Ghent, Belgium
1968 - 1971	Graduate Assistant, University of Michigan, Ann Arbor, Michigan
1970 (Summer)	Lawrence Radiation Laboratory, Livermore, California
1963 - 1968	Science and Mathematics teacher, Classical High School, Providence and Barrington College, Barrington, Rhode Island

<u>PROFESSIONAL
SOCIETY
MEMBERSHIPS</u>:   American Chemical Society
American Association for the Advancement of Science
American Meteorological Society
Gesellschaft für Aerosolforschung

<u>PUBLICATIONS</u>:

     JR = Journal article, refereed
JNR = Journal article, nonrefereed
  P = Popular article
 CH = Chapter of book
 CP = Conference proceedings
  R = Report

JR   Dams R., Robbins J.A., Rahn K.A. and Winchester J.W. (1970) Nondestructive neutron activation analysis of air pollution particulates. <u>Anal. Chem.</u> <u>42</u>, 361.

CP   Dams R., Rahn K.A., Robbins J.A., Nifong G.D. and Winchester J.W. (1971) Multi-element analysis of air pollution particulates by nondestructive neutron activation. Proceedings of the Second International Clean Air Congress, eds. H.M. Englund and W.T. Beery, pp. 509-516. Academic Press, New York.

JR   Harrison P.R., Rahn K.A., Dams R., Robbins J.A., Winchester J.W., Brar S.S. and Nelson D.M. (1971) Areawide trace metal concentrations in Northwest Indiana as determined by multielement neutron activation analysis: a one-day study. J. Air Poll. Contr. Assoc. 21, 563.

JR   Rahn K.A., Dams R., Robbins J.A. and Winchester J.W. (1971) Diurnal variations of aerosol trace element concentrations as determined by nondestructive neutron activation analysis. Atmos. Environ. 5, 413.

JR   Dams R., Rahn K.A., Nifong G.E., Robbins J.A. and Winchester J.W. (1971) Nondestructive multielement analysis of air pollution particulates. Isotopes and Radiation Technology 9, 54.

JR   Rahn K.A., Wesolowski J.J., John W. and Ralston H.R. (1971) Diurnal variations of aerosol and trace element concentrations in Livermore, California. J. Air Poll. Contr. Assoc. 21, 406.

CP   Dams R., Robbins J.A., Rahn K.A. and Winchester J.W. (1971) Quantitative relationships among trace elements over industrialized Northwest Indiana. In: Nuclear Techniques in Environmental Pollution, International Atomic Energy Agency, Vienna.

JR   Dams R., Rahn K.A. and Winchester J.W. (1972) Evaluation of filter materials and impaction surfaces for nondestructive neutron activation analysis of aerosols. Env. Sci. Technol. 6, 441.

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